AQUEOUS AND SOLID PHASE INTERACTIONS OF RADIONUCLIDES WITH ORGANIC COMPLEXING AGENTS

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PhD 2019

Aqueous and solid phase interactions of radionuclides with organic complexing agents

by

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A thesis submitted to the University of Plymouth in partial fulfilment for the degree of

Doctor of Philosophy

School of Geography, Earth and Environmental Sciences

Faculty of Science and Technology

September 2010

Abstract

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Estela Reinoso-Maset

Characterising the geochemistry and speciation of major contaminant radionuclides is crucial in order to understand their behaviour and migration in complex environmental systems. Organic complexing agents used in nuclear decontamination have been found to enhance migration of radionuclides at contaminated sites; however, the mechanisms of the interactions in complex environments are poorly understood. In this work, radionuclide speciation and sorption behaviour were investigated in order to identify interactions between four key radionuclides with different oxidation states (Cs(I) and Sr(II) as important fission products; Th(IV) and U(VI) as representative actinides), three anthropogenic organic complexing agents with different denticities (EDTA, NTA and picolinic acid as common co-contaminants), and natural sand (as simple environmental solid phase).

A UV spectrophotometric and an IC method were developed to monitor the behaviour of EDTA, NTA and picolinic acid in the later experiments. The optimised methods were simple, applied widely-available instrumentation and achieved the necessary analytical figures of merit to allow a compound specific determination over variable background levels of DOC and in the presence of natural cations, anions and radionuclides.

The effect of the ligands on the solubility of the radionuclides was studied using a natural sand matrix and pure silica for comparison of anions, cations and organic carbon. In the silica system, the presence of EDTA, NTA and, to a lesser extent, picolinic acid, showed a clear net effect of increasing Th and U solubility. Conversely, in the sand system, the sorption of Th and U was kinetically controlled and radionuclide complexation by the ligands enhanced the rate of sorption, by a mechanism identified as metal exchange with matrix metals. Experiments in which excess EDTA, NTA and picolinic acid (40 – 100 fold excess) were pre-equilibrated with Th and U prior to contact with the sand, to allow a greater degree of radionuclide complex formation, resulted in enhanced rates of sorption. This confirmed that the radionuclide complexes interacted with the sand surface more readily than uncomplexed Th or U. Overall this shows that Th and U mobility would be lowered in this natural sand by the presence of organic co-contaminants. In contrast, the complexation of Sr with the complexing agents was rapid and the effect of the ligands was observed as a net increase on Sr solubility (EDTA, picolinic acid) or sorption (NTA). As expected, Cs did not interact with the ligands, and showed rapid sorption kinetics.

Finally, ESI-MS was used to study competitive interactions in the aqueous Th-Mn-ligand ternary system. Quantification presented a challenge, however, the careful approach taken to determine the signal correction allowed the competitive interactions between Mn and Th for EDTA to be studied semi-quantitatively. In an EDTA limited system, Th displaced Mn from the EDTA complex, even in the presence of a higher Mn concentration, which was consistent with the higher stability constant of the Th-EDTA complex.

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Acknowledgments

I cannot finish the last typing of my thesis in a better way than acknowledging the people who have made my whole PhD an experience to always remember.

First and foremost, I would like say the most sincere and deepest thanks to my two supervisors Miranda Keith-Roach and Paul Worsfold, who through these 4 years of lab work and writing-up, have given me the opportunity to learn what research is, and made me discover that I can also do science. Miranda, your endless energy and encouragement are contagious and have always taken my tears of frustration away. Paul, never stressed up man, your "are you free for 5 minutes?" chats and "red pen" writing give priceless advice. You both have taught me many things, but above all, that we can always get a story...and definitely a good one!

I would also like to thank the technicians in Davy Building, especially the 3 Andys - Fisher, Arnold and Tonkin, who by looking after the instruments, labware and students make the time in the lab easy and enjoyable. Thanks to Colin May for his help at my beginnings with the electrospray and to Geoff Millward too, for the always constructive and interesting talks (and sometimes even laughs) in and out of the lab.

Colleagues and friends have been, and will always be, part of this story. And like the story chapters, they have contributed to it at different stages – starting from the five Spanish men Antonio, Juan, Juan II, Jose and Quique, to the half-Spaniard Fay and the "adopted" Spaniards Yaswant and Gerald, and more recently the inseparable Patricia and Alba, all always ready to party and take me dancing! Quieter times at coffee and lunch breaks have also been great mind escapes, mainly in the company of pasty man Colin, perfect tea maker Bernhard, Anders – gotta keep walking!, Jinbo (+ fish and crabs), my lovely friend Kerstin, sun-lover Rachel, Alison (that gift list still in my labcoat pocket), smiley Alex, my favourite *identical twins* Rob (Runcan for most) and Luke (who also put music to my writing), and, especially in the last year and a half, in the company of my most competitive friend Jan – I know, you've won...again!

I can't forget to say a big thanks to my lab and conference partner Jane, for always being up for listening to my talk once again, to my deskmate and fantastic friend Marie for always being there when I needed, and to Leyla for sharing birthday parties and true writing-up frustrations – despite some tears, we all certainly get there Leyla...no difference for you!

Finally, I would like to dedicate the last words to my boyfriend Sebas, who has been so supportive during the last year (or two), patiently listened my scientific unintelligible thoughts, and had so many lonely dinners...I can now cook for you again, *chuliño*!

Author's declaration

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award without prior agreement of the Graduate Committee.

This study was financed with the aid of a studentship from Nexia Solutions Limited (Agreement Number 1002373).

Relevant scientific seminars and conferences were regularly attended at which work was presented; and papers were prepared for publication.

The work presented in this thesis was primarily the work of the author unless acknowledged otherwise.

Word count of main body of thesis

25,502 *words*

Signed: .....

Date: 15/12/2010

Presentations

ORAL

2010 – "Is EDTA able to solubilise Th in real environments?" *Reinoso-Maset, E., May, C. C., Worsfold, P. J., & Keith-Roach, M. J.*, presented at:

* 11th International Symposium on Environmental Radiochemical Analysis 2010, Best Western Queen Hotel, Chester, UK, 15th – 17th September 2010.
* Young Researchers Meeting 2010, Royal Society of Chemistry – Radiochemistry Group, Burlington House, London, UK, 14th April 2010.
* COGER Annual Meeting 2010, University of Lancaster, Lancaster, UK, 29th – 31st March 2010.

2009 – "Exploring ternary interactions between radionuclides, organic complexing agents and natural sand" *Reinoso-Maset, E., Worsfold, P. J., & Keith-Roach, M. J.*, presented at:

* MIGRATION '09, 12th International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Three Rivers Convention Centre, Kennewick, Washington, USA, 20th – 25th September 2009.
* COGER Annual Meeting 2009, University of Liverpool, Liverpool, UK, 6th – 8th April 2009.

2008 – "Radionuclides, organic complexing agents and solid phases: exploring their interactions" *Reinoso-Maset, E., Worsfold, P. J., & Keith-Roach, M. J.*, presented at:

* Goldschmidt 2008, University of British Columbia, Vancouver, Canada, 13th – 18th July 2008.
* Young Researchers Meeting 2008, Royal Society of Chemistry – Radiochemistry Group, Burlington House, London, UK, 16th April 2008.

* COGER Annual Meeting 2008, University of Nottingham, Nottingham, UK, 7th – 10th April 2008.
* Nexia Solutions – Environmental Process Symposia, University of Sheffield, Sheffield, UK, 7th February 2008.

2007 – "Radionuclide speciation and solubility in the presence of organic complexing agents and soil components" *Reinoso-Maset, E., Worsfold, P. J., & Keith-Roach, M. J.,* presented at:

* COGER Annual Meeting 2007, University of Loughborough, Loughborough, UK, 17th – 19th April 2007.

POSTER

2008 – "Impact of co-contaminant complex speciation on radionuclide sorption to sand" *May, C. C., Reinoso-Maset, E., Worsfold, P. J., & Keith-Roach, M. J.,* presented at:

* 2nd International Nuclear Chemistry Congress, Cancun, Mexico, 13th – 18th April 2008.

2007 – "Radionuclide speciation and solubility in the presence of organic complexing agents using electrospray ionisation mass spectrometry" *Reinoso-Maset, E., Worsfold, P. J., & Keith-Roach, M. J.,* presented at:

* Royal Society of Chemistry – Analytical Research Forum 2007 (ARF07), University of Strathclyde, Glasgow, UK, 16th – 18th July 2007.

Dedicated to my parents, Manolo & MariLuz,

and to my grandparents, Antonio & Matilde and Leonardo & Francisca.

Caminante, son tus huellas
el camino y nada más,
caminante, no hay camino,
se hace camino al andar.

Al andar se hace camino
y al volver la vista atrás
se ve la senda que nunca
se ha de volver a pisar.

Caminante no hay camino
sino estelas en el mar...

Traveller, your footsteps are
the path, and nothing else.
Traveller, there is no path,
the path is made as you walk.

By walking you make the path,
and looking back
you see the trail
never to be trod again.

Traveller, there is no path,
only wakes on the sea...

- Antonio Machado -

Chapter 1

Introduction

1.1 Nuclear waste and contaminated land

With 437 nuclear power reactors in operation worldwide and 55 under construction at the end of 2009 (IAEA, 2010), the production of nuclear energy is in a state of constant growth and currently represents 13.5 % of the total electricity generated in the world (OECD/IEA, 2010). Consequently, the management of radioactive waste produced during the different stages of the nuclear fuel cycle represents one of the great environmental challenges worldwide.

Figure 1.1 shows the origin and management of radioactive waste at UK nuclear power plants (NDA, 2009). Radioactive waste is classified as high, intermediate or low level depending on the specific activity and the heat produced through radioactive decay. As shown in Figure 1.1, the classification affects the management approach taken to minimise the volume of waste and reduce its potential hazard. To ensure safe handling during transportation, storage and final disposal, the waste is generally converted into a stable solid form which immobilises the radionuclides and provides containment (NDA, 2009; www.world-nuclear.org). The final step of all management routes involves land-based disposal, either in a near surface repository or a deep geological facility, where the waste can be isolated and stored until the radiological impact on the biosphere is negligible (IAEA, 2009). In the UK, low level waste (LLW) is currently disposed of at the near surface waste facility in the vicinity of Drigg (Cumbria). However, in the absence of a repository for the disposal of the UK's high and intermediate level waste (HLW, ILW), these wastes are often stored at the site of generation (NDA, 2006). Although no country has an operational deep geological repository, countries such as Sweden, Finland and USA

have selected the location of their repository and started the long process of public acceptance (www.world-nuclear.org).

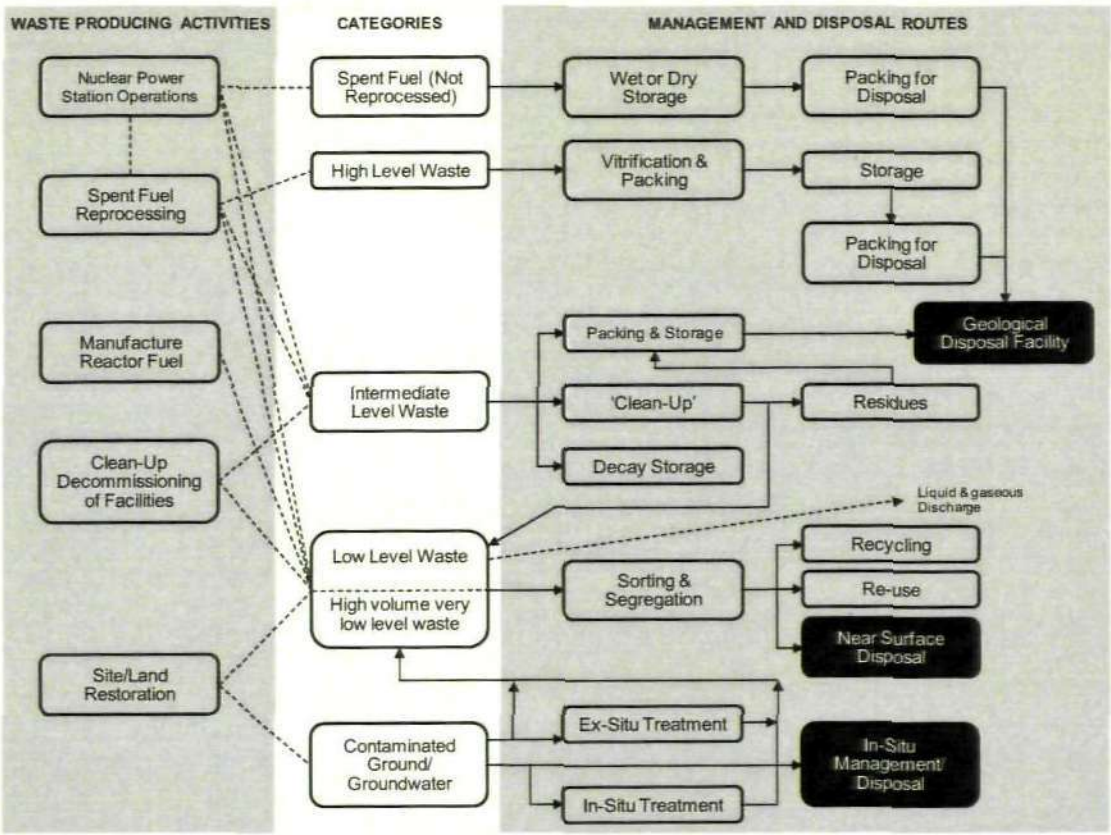

Figure 1. 1 Origin and management of radioactive waste in the UK adapted from NDA (2009). Black boxes highlight the land-based radioactive waste disposal.

The major risk associated with geological disposal is that a combination of unpredictable circumstances could lead to the rupture of protective barriers around the waste containers, followed by dissolution and transport of the most hazardous products (Choppin *et al.*, 2002). The leakage of radionuclides from the waste repository and their migration through the surrounding environment via a water transport pathway depends greatly on subsurface water flow rates (Haszeldine & McKeown, 1995), and is more likely to be significant for radionuclides with long half-lives, high solubilities in groundwater and low sorption to soils (Choppin *et al.*, 2002).

The management of radioactive waste is at present regulated by national policies with international standards, guidelines and recommendations from, for example, the International Atomic Energy Agency (IAEA) (www.world-nuclear.org). However, during the early development of the military and civil applications of nuclear power, regulations were weaker and poor practices resulted in contamination of licensed sites. Examples of contaminated sites include Oak Ridge National Laboratory (TN, USA), which was established in 1943 for producing and separating plutonium for nuclear weapons as part of the Manhattan project (www.ornl.gov, 2010). Major releases from shallow, unlined disposal trenches have been identified here and are known to have contaminated the groundwater with the transuranic radionuclides ^{244}Cm and ^{241}Am (McCarthy *et al.*, 1998). The US Department of Energy's Hanford Reservation (WA, USA) provides another example where land has become contaminated through direct disposal to ground and leaks of complex mixtures of radioactive and hazardous wastes from aging underground tanks (Bryan & Siegel, 2003). These inputs of contaminants to the subsurface have resulted in the movement of contaminants (e.g. Cr, ^{90}Sr, ^{99}Tc, U, ^{60}Co, ^{137}Cs) through the vadose zone into the groundwater, leading to a contaminated area of approximately 183 km^2 (about 12 % of the 1450 km^2 total site area), and some radioisotopes have reached the adjacent Columbia River (Hartman *et al.*, 2009; Pace *et al.*, 2007; Serne & LeGore, 1996). The Chalk River Nuclear Laboratories in Canada was also involved in the Manhattan project and this were the site of the first nuclear reactor built outside of the USA, in 1945. The low level wastewater disposal pit constructed in the mid 1950s has released ^{60}Co to the groundwater, which has migrated to adjacent wetland (Killey *et al.*, 1984).

Important sources of contamination outside North America include the nuclear weapon production facility of the Mayak Chemical Combine in Russia, which discharged medium level liquid waste produced between 1948 and 1951 directly into the Techa River, Lake Karachay and small nearby lakes. The leakage of radionuclides from the lakes has produced a groundwater plume that extended 2.5 – 3.0 miles from the lake and left a legacy of > 4 Mm^3 of contaminated groundwater with long-lived fission products (Bryan & Siegel, 2003). In the UK, Britain's first nuclear reactor and the associated reprocessing plant (to separate U and Pu from fission products) were launched in 1947 at what is now the Sellafield site (Cumbria) and the first power generation reactors followed on the 1950s. These facilities have been used for the temporary storage of solid and liquid reprocessing wastes, and a number of leaks of radioactive fluids to ground from plant buildings, vaults and disposal trenches are known to have occurred (Hunter, 2004). This has left up to 20 million m^3 of contaminated ground and distinct contaminated groundwater plumes containing ^{90}Sr, ^{137}Cs, ^{3}H and ^{99}Tc (Hunter, 2004; Reeve & Eilbeck, 2007). Therefore, radioactively contaminated land is a global issue that is of great relevance to the UK.

Intentional or unpredicted releases into the biosphere can ultimately result in radionuclides reaching humans via the major transfer routes shown in Figure 1.2. Therefore, understanding the behaviour and migration of radionuclides from waste repositories and contaminated sites into the biosphere is essential to minimise and predict the impact of possible releases on the environment and, consequently, on human health.

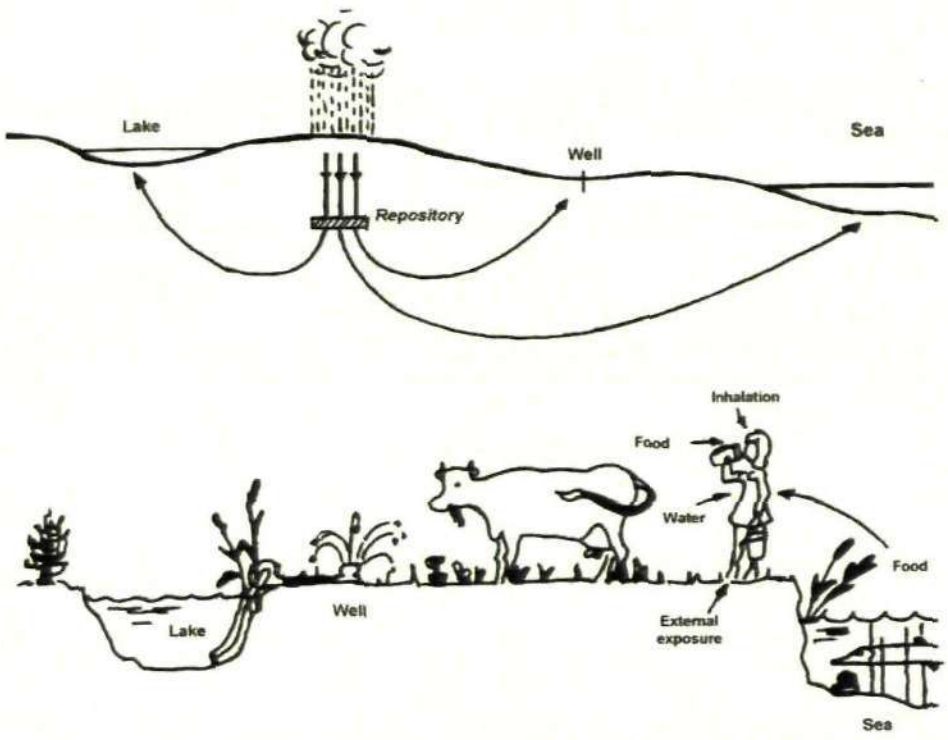

Figure 1. 2 Migration path of radioactive nuclides from waste repository to man (adapted from Choppin *et al.* (2002)).

1.2 Fission products and actinides produced during nuclear energy production

Hundreds of fission products are produced during the fission of ^{235}U, and the most abundant fission products have atomic masses around 95 and 135 with yields between 6 – 7 %. These include ^{90}Sr, ^{93}Zr, ^{99}Tc, ^{107}Pd, ^{134}Cs, ^{137}Cs. Neutron capture also occurs in nuclear fuel and the most important neutron capture reaction involves the abundant ^{238}U isotope (~97 % of the fuel), creating ^{239}U. This short-lived U isotope ($t_{1/2}$ = 23.5 min) decays to ^{239}Np ($t_{1/2}$ = 2.36 days) which in turn decays to ^{239}Pu. Plutonium 239 is fissile and thus contributes to energy production but can also form heavier isotopes through further neutron capture reactions. Therefore fission products and actinides are important

components of spent fuel (Table 1.1). In general, medium-lived fission products represent the major radiation hazard over the first three hundred years after disposal. However, the long term hazard comes from long-lived fission products, such as ^{99}Tc, ^{129}I, ^{93}Zr, and actinides.

Table 1. 1 The main radionuclides occurring in radioactive waste from the nuclear cycle, their half-lives, type of radiation and % in weight present in the spent fuel (Milnes, 1985). *The % of total activity was calculated from two specific examples of inventories of the longer-lived radionuclides present in UK intermediated-level and high-level waste after approximately 10 and 1000 y disposal respectively (Chapman & McKinley, 1987). No data indicates that the radionuclide was not present or its contribution was negligible.

Radionuclide	Half-life (y)	Type of radiation	% Weight in spent fuel	% of total activity*	
				10 y	1000 y
Fission Products					
^{90}Sr	28.5	β	0.09	27	
^{93}Zr	1 000 000	β	-		15
^{99}Tc	210 000	β	-	0.01	61
^{107}Pd	6 500 000	β	-		0.59
^{129}I	16 000 000	β	0.30		0.15
^{135}Cs	2 000 000	β	} 0.28		1.36
^{137}Cs	30.1	β		36	
Actinides					
^{230}Th	75 400	α	-		0.0014
^{232}Th	14 100 000 000		-		
^{234}U	240 000	α	-		0.15
^{235}U	710 000 000	α	0.76		0.0005
^{236}U	24 000 000	α	0.42		0.01
^{238}U	4 500 000 000	α	94.2		0.01
^{237}Np	2 100 000	α	0.05		
^{238}Pu	87.7	α	0.02	0.15	
^{239}Pu	240 000	α	0.53	0.50	
^{240}Pu	6 540	α	0.22	0.52	
^{241}Pu	14.4	α	0.10	23	
^{242}Pu	380 000	α	0.04		
^{241}Am	433	α	-	1.34	
^{243}Am	7 400	α	0.02		

Key radioisotope contaminants at nuclear sites clearly reflect the isotopes that are important in spent fuel. Caesium, Sr, Th and U have been selected for this study; thus their environmental chemistry is introduced briefly here. Caesium and Sr each occur in one oxidation state, Cs(I) and Sr(II), and have a low tendency to interact with inorganic or organic ligands in soil/water environments (EPA, 1999). Therefore, their aqueous speciation is dominated by Cs^{+} and Sr^{2+} cations in most groundwater systems. Caesium is rapidly and strongly sorbed by ion-exchange into clay interlayer sites and, when this causes the collapse of the interlayers, Cs is irreversibly sorbed (Bryan & Siegel, 2003). Strontium is also rapidly sorbed but remains largely exchangeably bound to soils (Serne & LeGore, 1996). The importance of ion exchange processes means that Cs and Sr retention in soils is strongly influenced by the ionic strength of the pore water, and in natural waters, K^{+} and Ca^{2+} effectively compete with Cs^{+} and Sr^{2+} respectively for the ion exchange sites, and thus increase their mobility (Bryan & Siegel, 2003; Keith-Roach & Livens, 2002).

Uranium is the major component of nuclear waste and thus one of the most important actinides in terms of risk assessment. It is also the most abundant of the naturally occurring actinides and can exist in the III, IV, V and VI oxidation states, of which IV and VI are the most common states found in the environment (Cotton & Wilkinson, 1988). The U(IV) species dominate under reducing conditions and have a low solubility, whereas the oxidised U(VI) species, UO_2^{2+}, is much more mobile and soluble in most geochemical systems. Thorium is also a naturally occurring radionuclide but exists solely in the IV oxidation state, under all redox conditions. Its isotopes are part of the uranium-decay series and hence environmentally important. Furthermore, Th(IV) is used as a chemical

analogue for other tetravalent actinides with higher specific activities in order to reduce handling hazards and/or to reduce the complexity of working with redox active actinides. In pure aqueous solution, both U(VI) and Th(IV) readily hydrolyse (Choppin, 2006; Santschi *et al.*, 2006) and at neutral to basic pH carbonate complexes are the dominant form of U and, to a lesser extent, Th (Choppin, 2006; Echevarria *et al.*, 2001; Santschi *et al.*, 2006). Both actinides are complexed significantly by organic ligands, such as fulvic and humic acids and anthropogenic complexing agents (Cartwright *et al.*, 2007; Murphy *et al.*, 1999), thus enhancing their environmental solubility.

Table 1.2 summarises the chemistry of these four key radionuclides in nuclear waste. The contrasting differences between the chemistry of these fission products and actinides highlight the importance of studying their environmental behaviour at contaminated lands in nuclear sites.

Table 1. 2 Radionuclides of interest and their main chemical characteristics.

Rad.	Oxid. states	Solubility	Main species in solution	Complexation		Sorption
				Inorganic	*Organic*	
Cs	I	High	Cs^{+}	Very weak/None	Very weak/None	Strongly to clays, irreversible
Sr	II	Relatively high	Sr^{2+} (pH 3 - 10)	Weak (SO_4^{2-}, CO_3^{2-}, Cl^{-}, NO_3^{-})	Weak	Strongly to clays, exchangeable
Th	IV	Low	Th^{4+} (pH < 3); Hydroxyl (pH > 3)	Fair (F^{-}, PO_4^{2-}, Cl^{-}, NO_3^{-})	Strong (humics, polycarboxylic acids)	Strongly to clay and oxides; important to silica only at pH 3 - 6
U	IV, VI	High	UO_2^{2+} (pH < 6) Carbonates (pH > 6)	Very strong with CO_3^{2-}	Considerable	Strongly to clay and oxides; poor at alkaline conditions; highly pH dependent

1.3 Organic complexing agents

The ability of organic ligands to complex and solubilise metal ions results in their wide industrial use, e.g. to inhibit reactions catalysed by metals, avoid the formation of low-solubility metal salt precipitates and aid in the removal of previously formed deposits (Reemtsma & Jekel, 2006). Synthetic complexing agents of the aminopolycarboxylate type, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), are characterised by the presence of several carboxyalkyl groups bound to one or more nitrogen atoms in their structure (Figure 1.3 A and B). The nitrogen and the deprotonated, negatively charged oxygen of carboxylic acid groups are potential ligand atoms (i.e. with electron donor characteristics) that are able to bind metal ions in ring structures, and therefore form stable and highly water soluble metal complexes. The stability of the complexes formed generally increases with the number of available nitrogen and carboxylic oxygen atoms in the ligand (Reemtsma & Jekel, 2006). Heterocyclic carboxylic acids, such as picolinic acid (Figure 1.3 C), also have the potential to act as ligands by coordination of the carboxylate oxygen atom and the ring heteroatom, i.e. nitrogen for picolinic acid (Silverwood *et al.*, 1998).

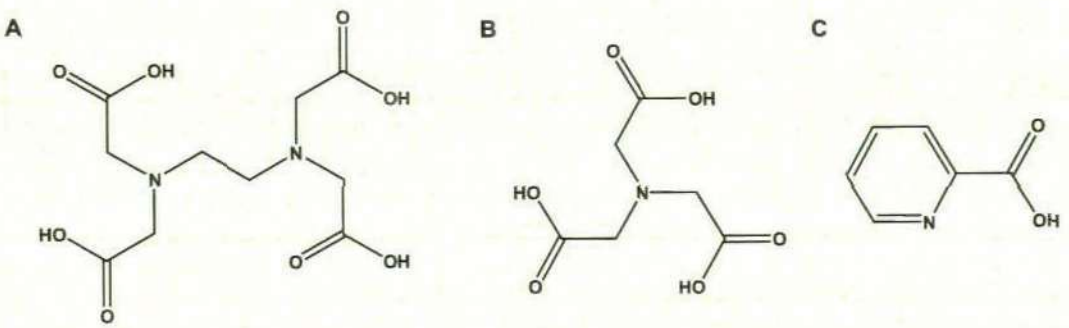

Figure 1. 3 The chemical structures of **A**) EDTA, **B**) NTA and **C**) picolinic acid.

These ligands have also been used widely in nuclear waste reprocessing (Baisden & Choppin, 2007) and as solvents, degreasing agents, purification and decontamination agents and flocculating agents at nuclear sites (Riley & Zachara, 1992; Toste *et al.*, 1988). Organic complexing agents such as EDTA, NTA and picolinic acid have therefore been co-disposed in nuclear waste and are commonly found in radioactive contaminated land (Delegard *et al.*, 1984; Killey *et al.*, 1984; McIsaac *et al.*, 1992; Means *et al.*, 1978; Piciulo *et al.*, 1986; Riley & Zachara, 1992; Toste *et al.*, 1988). For example, 3.6×10^{-3} M EDTA solutions were periodically disposed of to the Hanford process ponds from 1943 to 1974 (Riley & Zachara, 1992). The analysis of a cladding sludge and a volume reduction slurry waste revealed the presence of high concentrations of EDTA in the solid phase of the waste (414 and 52.8 $\mu g\ g^{-1}$), while NTA was present at a much lower concentration (trace and 5.8 $\mu g\ g^{-1}$) (Toste *et al.*, 1988). Laboratory studies have used concentrations of 11.8 - 31×10^{-3} M (Kocherginsky *et al.*, 2002; Toste *et al.*, 1995; Toste *et al.*, 2005) and 7.3×10^{-3} M (Toste *et al.*, 1995) to simulate EDTA and NTA, respectively, in Hanford wastes. At Oak Ridge National Laboratory, 3.7×10^{-7} M EDTA was measured in groundwater that had been contaminated from nearby pits and trenches (Riley & Zachara, 1992). The picolinic acid concentration in waste from FiztPatrick Nuclear Power Station (NY, USA) was determined to be at least 2.2 % m/m (McIsaac *et al.*, 1992).

The co-disposal of organic complexing agents in radioactive waste has resulted in enhanced migration of radionuclides through contaminated sites. EDTA was implicated in the migration of radionuclides, principally ^{60}Co, up to several meters from two radioactive waste burial trenches at Oak Ridge National Laboratory (Killey *et al.*, 1984; McCarthy *et al.*, 1998; Means & Alexander, 1981; Means *et al.*, 1978). The mobilisation of ^{239}Pu and ^{238}Pu

from trench leachates at the Maxey Flats radioactive waste disposal sites (KY, USA) was also associated with EDTA complexation (Cleveland & Rees, 1981). Therefore, the role of co-disposed organic complexing agents on radionuclide mobility and their interactions with radionuclides in the host environment is of high environmental relevance at nuclear sites and contaminated land.

1.4 Interactions of radionuclides and organic complexing agents with solid phases

Sorption processes are a fundamental factor in controlling radionuclide mobility and hence migration, in the host environment. Radionuclide sorption occurs as a function of the solid phase, i.e. mineralogy, particle size, concentration of sorbed ions and surface sites. Solution phase characteristics, i.e. pH, ionic strength and cation concentration, also play an important role in controlling the sorption of radionuclides to solid phases. The chemistry of a given radionuclide controls its solid phase associations and the effects driven by changes in the solution phase. For example, increased ionic strength reduces sorption of Cs to clays (Flury *et al.*, 2004; Poinssot *et al.*, 1999), but does not affect Th(IV) sorption to TiO_2 (Jakobsson, 1999) or silica (Chen & Wang, 2007b). pH is a particularly important control, because it influences the speciation of the radionuclide and the charge on the solid phase surface. For example, an increase in pH from 1 to 4 significantly enhances Th sorption to TiO_2 (Jakobsson, 1999), hematite (α-Fe_2O_3) (Reiller *et al.*, 2005), alumina (γ-Al_2O_3) (Chen & Wang, 2007a) and silica (SiO_2) (Chen & Wang, 2007b; Osthols, 1995).

In real environmental systems, dissolved organic ligands can also modify the solution phase characteristics and radionuclide interactions with the solid phase. Figure 1.4 summarises possible interactions between radionuclides, ligands and solid phases.

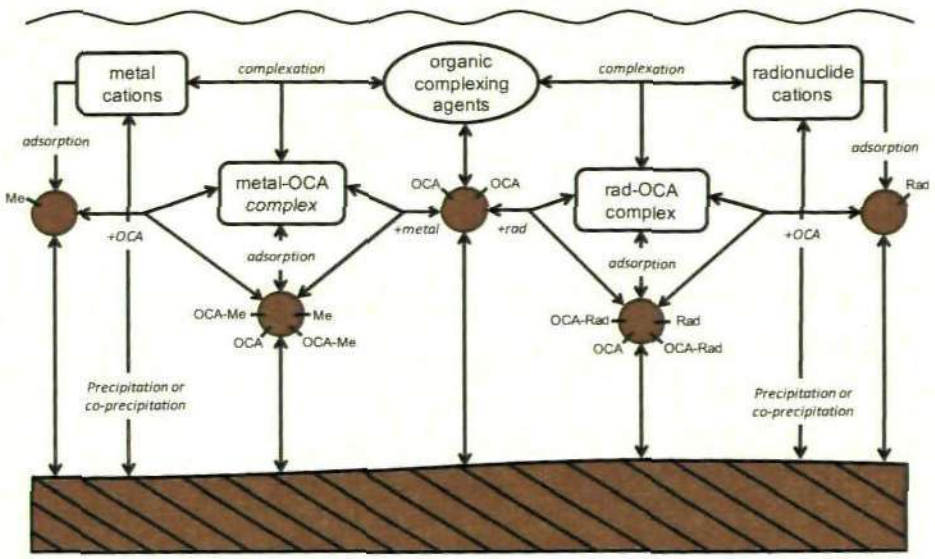

Figure 1. 4 Possible interactions of dissolved radionuclides (rad) and metal cations with organic complexing agents (OCA) in the presence of a solid phase.

The extent to which organic ligands affect radionuclide mobility through complexation is controlled by the stability constants of the complexes. The stability constant (*k* or log *k*) is the equilibrium constant for the complexation reaction, and high stability constants reflect stable complexes. EDTA complexes are generally stable, due to the hexadentate nature of the ligand. However, studies involving a range of radionuclides and metals in diverse environments have shown contrasting results. Certainly, EDTA has been linked to the enhanced migration of ^{60}Co and ^{239}Pu and ^{238}Pu at contaminated sites (Means & Alexander, 1981; Means *et al.*, 1978), and has been found to promote actively U migration through intact sandstone cores (Read *et al.*, 1998) and to reduce the sorption of Co, Sr and Am to sediment efficiently (Delakowitz & Meinrath, 1998; Delegard *et al.*, 1984). The formation of Cu-picolinic acid complexes (Davis & Leckie, 1978) has also been

reported to prevent the sorption of Cu onto amorphous iron oxide from pH 4 – 7. Conversely, in other systems, the presence of organic ligands has been found to have either no effect on radionuclide and metal mobility or to enhance sorption. Serne *et al.* (2002) observed no change in the sorption of U(VI) and Th(IV) to a synthetic Fe-coated sand, or to a natural sandy soil, in the presence of equimolar EDTA or picolinic acid (10^{-5} M) over a pH range of 4 – 10, reflecting a lack of significant radionuclide-ligand complex formation. Pathak & Choppin (2007) also found that up to 10^{-3} M EDTA did not complex UO_2^{2+} (5×10^{-5} M) significantly in the presence of silica gel and hence had no effect on the sorption profile of U in the pH range 3 – 6. Th(IV) solubility was unaffected by increasing concentrations of EDTA (0.1 – 0.5 M) at pH 3 (Cetiner, 2007). EDTA was found to have no effect on Cs or Sr sorption to Hanford sediment (Delakowitz & Meinrath, 1998; Pace *et al.*, 2007). In the case of Sr, the Sr-EDTA complex became dissociated upon contact with the sediment, and many other soil cations (Mg, Mn and Pb) formed stronger complexes with EDTA, leaving free Sr^{2+} which was sorbed by the sand fraction of the sediments (Pace *et al.*, 2007). Equimolar NTA (1 μM) did not modify Co sorption to gibbsite at pH < 7.5, but at higher pHs, a slight increase on sorption suggested the formation of a ternary $CoNTA^-$ surface complex (Girvin *et al.*, 1996). Enhanced sorption to aluminium oxide was also observed for low concentrations (10^{-6} M) of Ni- and Zn-EDTA complexes at pH < 6; however, at pH > 7, sorption became insignificant and thus complexation increased metal mobility (Bowers & Huang, 1987).

These contrasting observations reflect the complexity of radionuclide-organic complexing agent interactions and the importance of understanding speciation and sorption

processes to deduce the mechanisms by which co-disposed organic complexing agents can affect the solubility of radionuclides in a given system.

1.5 Determination of organic complexing agents

An accurate determination of organic complexing agents is essential in order to get a better understanding of their impact on radionuclide solubility and hence mobility. Dissolved organic carbon (DOC) analysis has been used as a surrogate measurement in laboratory experiments (Maset *et al.*, 2006; Pace *et al.*, 2007), but the natural DOC is dependent on the soil matrix and varies over time (Maset *et al.*, 2006). There is therefore a need for a compound-specific method of determination.

The absence of natural chromophore groups in both EDTA and NTA results in a low molar absorptivity (ε). However, their complexation with transition metals enhances the ε of the molecule, and thus spectrophotometric determination is feasible. Fe(III), Cu(II) and Co(II) have been used as complexing metals for the determination of EDTA, NTA and picolinic acid in pharmaceutical solution and cosmetics (Kemmei *et al.*, 2007; Kord *et al.*, 1995; Owens *et al.*, 2000; Pistos & Parissi-Poulou, 2002) as well as foods (Hamano *et al.*, 1993; Laamanen *et al.*, 2005b); and for more complex mixtures spectrophotometric detection has been coupled with ion chromatography (Piciulo *et al.*, 1986). It is also possible to use ion chromatography with suppressed conductivity detection for EDTA determination (Krokidis *et al.*, 2005), which has the advantage of not needing a derivatisation step. The limit of detection (LOD) ranged from 2 to 50 μM in these studies, depending on the metal

and method used, but all approaches allowed a compound-specific detection in a wide range of matrices.

1.6 Determination of radionuclides

Precise and accurate determination of radionuclides in environmental matrices is essential to study their environmental behaviour and migration. Radiometric methods have traditionally been used for the determination of radionuclides, which are based on detection of radioactive emissions. However, isotopes with long half-lives require long count times, and, with the exception of gamma analysis, time-consuming radiochemical separations are often required.

Inductively coupled plasma mass spectrometry (ICP-MS) is now frequently applied to the determination of long-lived radionuclides (Becker, 2003). The advantages of ICP-MS include excellent sensitivity at the ultratrace level and the ability to carry out precise isotope ratio measurements. Moreover, several isotopes can be determined simultaneously.

1.7 Determination of radionuclide-organic complexing agent aqueous speciation using ESI-MS

Determination of the aqueous speciation of radionuclide-organic complexes is key to understanding their behaviour and fate in the environment. Electrospray ionisation mass

spectrometry (ESI-MS) is able to provide stoichiometric information due to its soft mode of ionization which maintains solution phase speciation to a large extent as non-volatile solution species are transferred into the gas phase. ESI-MS also offers relatively high analytical sensitivity (Figure 1.5).

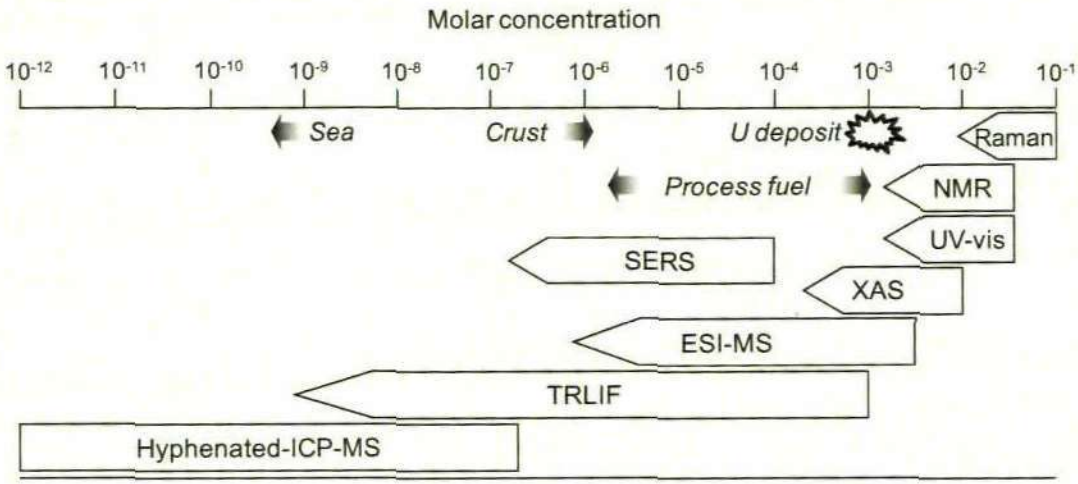

Figure 1. 5 Analytical techniques for the direct determination of radionuclide speciation, their working concentration ranges and approximate concentrations of U in different matrices for comparison (adapted from May *et al.* (2008)). [NMR = nuclear magnetic resonance spectrometry; UV-Vis = UV-visible spectroscopy; SERS = surface enhanced raman spectroscopy; XAS = X-ray absorbance spectroscopy; ESI-MS = electrospray ionisation mass spectrometry; TRLIF = time resolved laser induced fluorescence; ICP-MS = inductively coupled plasma mass spectrometry].

Figure 1.6 shows the three main steps of the electrospray process before the mass analysis. A solution containing the analyte of interest is pumped through an open ended stainless steel capillary (working electrode), which is held at high voltage, and sprayed towards the aperture plate (counter electrode). Under the influence of the applied field, ions of the same polarity as the voltage applied to the capillary tip travel towards the surface, while ions of the opposite polarity travel in the opposite direction and are retained in the capillary. When the accumulated charge at the liquid surface is sufficient to overcome the surface tension of the liquid, charged droplets are sprayed out from the

capillary. Solvent evaporation reduces the volume of the charged droplets, thus the charge density on the surface of each droplet increases until it becomes unstable, leading to fission of the droplets. This process repeats itself continuously, producing smaller and smaller droplets. Eventually the droplets contain a single charged species, so that on evaporation of the solvent gas-phase ions are formed that enter the mass analyser.

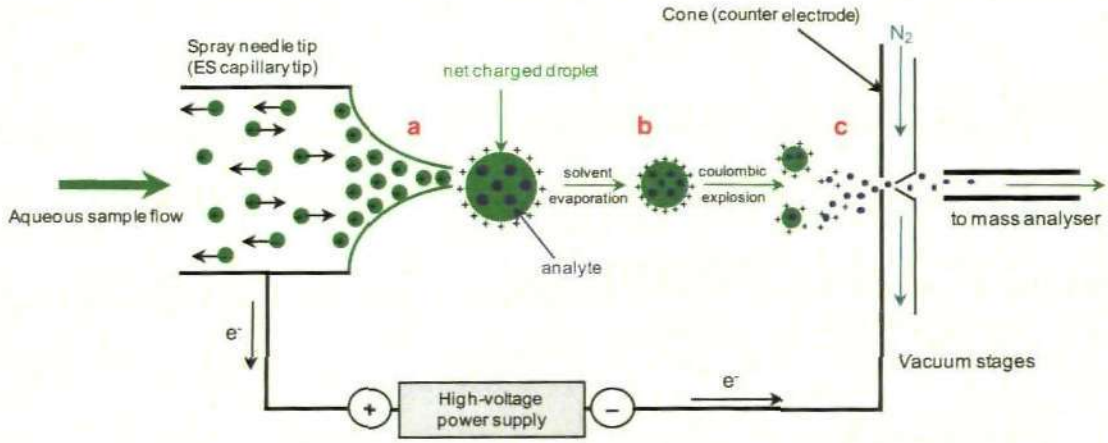

Figure 1. 6 Schematic representation of the processes occurring in the electrospray ion source operating in positive ion mode: **a**) generation of charged droplets, **b**) solvent evaporation and **c**) production of gas-phase ions.

The overall process allows the transfer of pre-existing ions, either positive or negative, from solution to the gas phase preserving their form and oxidation state. Therefore, the ESI-MS provides simple mass spectra with *m/z* peaks that relate directly to the species in solution. Other advantages of ESI-MS include the simultaneous detection of several species, and that a wide range of solvents can be used (from water to organic solvents) and a wide pH range can be tolerated (Keith-Roach, 2010).

Applications of ESI-MS include inorganic speciation (Agnes *et al.*, 1994; Stewart & Horlick, 1996), metal clusters (Agnes & Horlick, 1994a; Henderson *et al.*, 1998), inorganic (Wang & Agnes, 1999) and organometallic complexes (Henderson *et al.*, 1998; Ross *et al.*, 1998;

Ross & Luettgen, 2005) and organic substances (Crotti *et al.*, 2006). Keith-Roach (2010) summarises recent applications of ESI-MS to metal complex analysis in environmental, biological and chemical studies, and these include radionuclide and radionuclide complex speciation (Cartwright *et al.*, 2007; Keith-Roach *et al.*, 2005; Moulin *et al.*, 2001; Wang *et al.*, 2000). The identification and confirmation of metal complex formation and stoichiometry remains the main use within the ESI-MS studies. Relevant applications to this thesis, i.e. involving radionuclides and/or organic complexing agents, include the identification of La-EDTA complex and its dimer at pH 4.98 (Wang *et al.*, 2000), the confirmation of the complexation of Eu by diethylenetriaminepentaacetic (DTPA) and of Sr by EDTA and DTPA over the pH range 4 – 9 (Moulin *et al.*, 2003), the close examination of the U(VI)-citrate stoichiometry and structure (Somogyi *et al.*, 2007), the study of Th(IV) complexation by two siderophores over pH range 5 – 9 (Keith-Roach *et al.*, 2005) and the speciation of Th(IV) and U(VI) in the presence of EDTA and NTA over the pH range 2.5 – 10.8 (Cartwright *et al.*, 2007; May, 2009). The results were in good agreement with chemical equilibria calculations (Moulin *et al.*, 2003; Wang *et al.*, 2000), observations of *complementary techniques (Moulin et al., 2003) or previous experimental work* (Cartwright *et al.*, 2007; May, 2009) demonstrating the suitability of the ESI-MS for the study of radionuclide complex determination.

However, as reviewed in Keith-Roach (2010), quantification represents an important challenge for metal-complex analysis using ESI-MS. These problems mainly arise from different signal response between the different ions in solution due to the own characteristics of the species. However, the influence of instrumental set-up and other components in solution are also important. Baron & Hering (1998) found that the Cu- and

Pb-EDTA complexes gave lower signal intensities than uncomplexed EDTA, and Rellan-Alvarez *et al.* (2008) identified differences in signal intensity between Fe(II) and Fe(III) nicotinamine (NA) complexes due to the charge difference. Cartwright *et al.* (2007) observed that optimising the instrumental parameters significantly changed the total ion count of the three major peaks of Ca-isosaccharinate (ISA) species, and hence the distribution of the species. Rellan-Alvarez *et al.* (2008) observed that a higher capillary cone voltage increased the metal-ligand complex response, but the relative peak abundances also changed between the complexes. The addition of components to the system can also interfere with the quantification by suppressing the signal. For example, the addition of nitrate suppressed the signal intensity of two siderophores (Keith-Roach *et al.*, 2005) and metal salts suppressed the signal of metal aminopolycarboxylic acid complexes (Hotta *et al.*, 2009). The signal suppression may affect the species differently (Keith-Roach *et al.*, 2005); therefore, quantification of ternary systems can be complicated.

The use of another metal complex as internal standard has been successfully applied. For example, Co-EDTA and Ni-EDTA were used respectively by Hotta *et al.* (2009) and Wang & Agnes (1999) for the quantification of metal aminocarboxylate and Sr-EDTA complexes. External calibration can also be possible after accounting for signal suppression (Keith-Roach *et al.*, 2005) and by assuming that the measurements of the ion current in the gas phase quantitatively represented the solution equilibrium (Plancque *et al.*, 2005) and that there are equal signal responses for different charged complexes containing the same ligand (Baron & Hering, 1998; Plancque *et al.*, 2005). These assumptions were applied by Baron & Hering (1998) who used calibrations from single component aqueous

solutions to successfully quantify uncomplexed EDTA and Cu- and Pb-EDTA complexes in ternary systems by ESI-MS.

1.8 Aims and objectives

In order to understand the behaviour and migration of major contaminant radionuclides in complex environmental systems, their solubility and aqueous speciation in the host environment need to be better understood, particularly their interactions with anthropogenic organic complexing agents that are co-disposed of and/or found alongside radionuclides in nuclear waste and contaminated land. Therefore, the aim of this project was to obtain a detailed and mechanistic understanding of radionuclide interactions with organic complexing agents in the solution phase and in the presence of an environmental solid phase. Four key radionuclides with different oxidation states - Cs(I) and Sr(II) as important fission products, and Th(IV) and U(VI) as representative actinides; and three organic complexing agents with different denticities, EDTA, NTA and picolinic acid, were selected for the study. A natural sand was used as a simple environmental solid phase, representative of a high soil fraction in a variety of soil matrices. Radionuclide and organic complexing agent concentrations used throughout the study were within relevant concentrations of different contaminated scenarios (Hartman *et al.*, 2009; Riley & Zachara, 1992; Sylvester & Clearfield, 1998). The solid : solution ratio was selected to allow the determination of the processes taking place within a terrestrial environment in the presence of subsurface water. These experimental parameters were therefore of environmental relevance to radionuclide transport from radioactive waste repositories and in contaminated land.

The specific objectives of the project were to:

* adapt and optimise existing methods for the specific, direct and accurate determination of EDTA, NTA and picolinic acid in sand-water solutions;
* study the effect of EDTA, NTA and picolinic acid on Th(IV) solubility in the presence of a natural sand and elucidate the mechanisms of the sorption process;
* study and compare the effect of the three organic complexing agents on Cs(I), Sr(II) and U(VI) sorption to a natural sand under the same experimental conditions;
* assess ESI-MS as a quantitative tool in speciation studies of metal-ligand complexes and the extent to which it can be used to elucidate competitive interactions in the Th-Mn-EDTA ternary system;
* compare and discuss the experimental results with speciation model outputs and, consequently, evaluate how accurate predictions on radionuclide speciation and mobility in the presence of organic complexing agents can be made for competitive environmental systems.

Chapter 2

Method development for determining organic complexing agents by UV spectrophotometry and ion chromatography

2.1 Introduction

Organic complexing agents such as EDTA, NTA and picolinic acid are used in decontamination processes and have been found at nuclear sites (Means *et al.*, 1978). Their determination in natural samples and amended soil-water laboratory experiments is essential in order to obtain a better understanding of their effect on radionuclide fate and mobility in contaminated land. However, there is not a standard or established method for the determination of EDTA, NTA or picolinic acid in contaminated soil waters.

The aim of the research presented in this chapter was to adapt and optimise existing methods for the specific, direct and accurate determination of individual organic complexing agents (EDTA, NTA, picolinic acid) over a 5 – 200 μM concentration range in sand-water solutions. These sand-water solutions are experimentally obtained by mixing natural sand with ultrapure water (MilliQ) and will contain matrix cations (e.g. Ca, Fe) and anions (e.g. chloride, nitrate) as well as added radionuclide cations. Therefore, during the optimisation of a direct UV spectrophotometric method for picolinic acid and NTA, and an ion chromatography with suppressed conductivity detection method for EDTA, the following aspects were considered: i) simplicity and time of analysis, aiming for direct measurement of samples or minimal sample preparation; ii) identifying and minimising interferences; iii) suitable limits of detection to determine the organic complexing agent concentrations in sand-water solutions (see Chapters 3 and 4); and iv) the capability to distinguish the organic complexing agents from natural background DOC.

2.2 Experimental

2.2.1 Reagents and sample preparation

Sample preparation was carried out in an ISO 9001:2000 accredited laboratory. All chemicals used in the determinations were of analytical grade and ultra pure water obtained from a MilliQ purification system (Millipore, ≥ 18.2 MΩ cm^{-1}) was used for all solutions and sample preparation. All plasticware used was soaked in 2 % v/v Decon overnight, rinsed with MilliQ water, soaked in 10 % m/v hydrochloric acid (HCl) overnight and then rinsed again with MilliQ water. Plasticware was then left to dry in a laminar flow hood and stored in double zip lock plastic bags to avoid contamination.

Sodium EDTA and copper(II) chloride salts were obtained from Fisher Scientific (Loughborough, UK). NTA sodium salt, picolinic acid and iron(III) chloride salt were obtained from Sigma-Aldrich (Gillingham, Dorset, UK). Sodium chloride, sodium nitrate, potassium phosphate monobasic, sodium sulphate and sodium carbonate salts were from BDH Chemicals Ltd (Poole, England). Stock solutions were prepared in plastic centrifuge tubes by dilution of the respective salts, and to obtain the standard and sample concentrations, dilutions of the stocks were prepared in 6 mL plastic pots (UV spectrophotometry) or 1.5 mL glass vials (ion chromatography).

To assess the interferences from the natural background of DOC and dissolved ions in the experimental matrix used in Chapters 3 and 4, a sand-water mixture was prepared by mixing 10 mL of MilliQ water with 5 g of natural dune sand for > 24 h, centrifuging (3500 rpm, 6 min) and transferring the supernatant to a clean vessel. The standards were then prepared in this sand-water mixture solution. To investigate the effect of radionuclides on

the instrumental response to specific concentrations of the complexing agents, Th(IV) was selected from the radionuclides used throughout this study since it has the highest stability constants with the ligands (log $k_{[ThEDTA]}$ = 26.8; (Cartwright *et al.*, 2007)) . Thorium stock solutions were prepared from the nitrate salt (BDH Chemicals Ltd., Poole, England) and used within hours to minimise potential losses from precipitation.

2.2.2 Instrumentation

UV-visible spectrophotometry. Samples and standards were measured using a UV-Vis spectrophotometer (HP 8453 UV-visible system) with a quartz cuvette of 10 mm path length. Spectra were recorded over the wavelength range 190 – 900 nm and processed with HP UV-Visible ChemStation software.

Ion chromatography (IC). Samples and standards were analysed within 24 h using a Dionex DX-500 ion chromatography system (Dionex Co, Camberley, UK). Initial instrument conditions for anion determination are shown in Table 2.1.

Table 2. 1 Ion chromatographic conditions for anion and EDTA determination.

Instrument	Dionex DX-500
Eluent	*9 mM carbonate (pH 10.8)*
Columns	IonPac AS9-HC (4 x 250 mm); AG9-HC (4 x 50 mm)
Run time	< 15 min
Flow rate	*1 mL min^{-1}*
Injection loop	25 µL
Detection	Suppressed conductivity (ASRS-II), 100 mA current
System backpressure	*~ 2000 psi*
Background conductance	25-30 µS

2.3 Results and discussion

2.3.1 Picolinic acid determination

Picolinic acid has two distinct absorbance bands in the UV region (maxima at 211 and 265 nm). Therefore, a direct UV method was investigated for its determination. In order to select the best maximum absorbance wavelength (λ_{max}), six picolinic acid standards (0 – 100 µM) were prepared in MilliQ water and the spectra were recorded over the 200 – 300 nm wavelength range (Figure 2.1). The response was linear (R^2 > 0.999 for both wavelengths) but the sensitivity of the response was 25 % higher at 265 nm. The limit of detection (LOD = *3*standard deviation of the blank/slope*) for the 265 nm band was 0.10 µM.

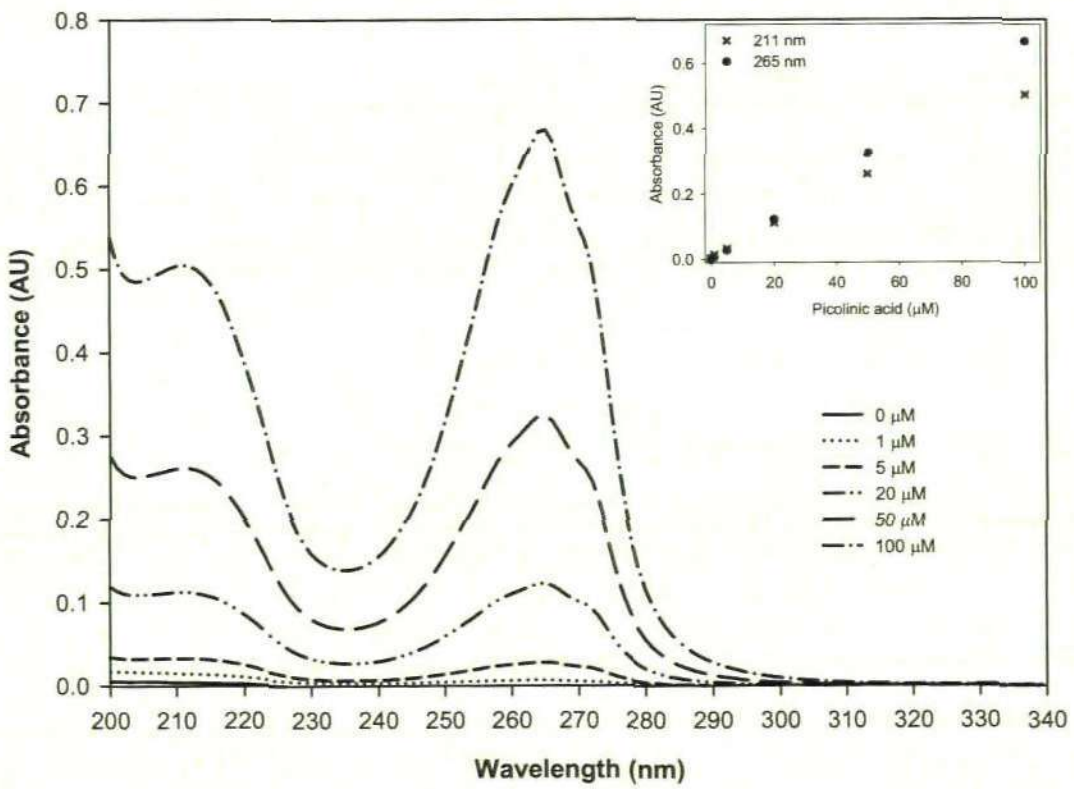

Figure 2. 1 UV spectra obtained for picolinic acid standards (0 – 100 µM) in MilliQ water. The instrumental blank was set using the 0 µM standard. Inset shows the calibration graph of picolinic acid at 211 and 265 nm.

Possible interferences. The absorbance could be affected by the presence of natural organic compounds or the radionuclides used in this study. In order to assess these interferences, three sets of 5 standards (0 – 100 μM) were prepared: i) in MilliQ water; ii) with 5 μM Th in MilliQ water and iii) in sand-water. The presence of Th, and thus the possible formation of Th-picolinic acid complexes, did not influence the LOD (< 0.10 μM), the sensitivity or the linear response (R^2 > 0.999). The sand-water matrix however gave a higher background in the UV region than MilliQ water, and this interfered with the signal from the picolinic acid standards as shown by a decrease in the gradient from 0.0067 to 0.0046 absorbance units per μM (AU μM^{-1}) and a significant increase in the LOD from 0.1 to 1.7 μM (Table 2.2). Preparation of the standards in sand-water diluted to 8 % of the original concentration with MilliQ water (i.e. 0.2 mL in 2.5 mL) reduced the background signal, and although the sensitivity was not improved, the response was linear (R^2 > 0.9991) and the LOD decreased to < 0.15 μM. Therefore, all subsequent analyses of samples and standards for picolinic acid were carried out after dilution to 8 % v/v with MilliQ water.

Table 2. 2 Characteristics of 5 point calibration graphs (0 – 100 μM) for picolinic acid in four different matrices.

Matrix	Gradient (AU μM^{-1})	Intercept (AU)	R^2	LOD (μM)
MilliQ water	0.0067	-0.0058	0.9998	0.10
MilliQ water + 5 μM Th	*0.0064*	*-0.0039*	*0.9999*	*0.02*
Sand-water	0.0046	0.0337	0.9957	1.74
8 % sand water	0.0043	-0.0027	0.9991	0.14

2.3.2 NTA determination

Selection of metal complexant. NTA does not contain a significant chromophore, thus metal complexation was needed to be able to apply a UV spectrophotometric method. Fe(III) or Cu(II) have been used in other studies, resulting in LODs within the range of 2 – 50 µM (Laamanen *et al.*, 2005b; Owens *et al.*, 2000). In order to select the best metal for this work, six NTA working standards (0 – 100 µM) were prepared in MilliQ water and 1 mM of Fe(III) or Cu(II) was added to each standard. Solutions were left to react for 2 h at room temperature and then the UV-visible spectrum (190 – 900 nm) was recorded. The λ_{max} for the Fe-NTA and Cu-NTA complexes were at 295 and 240 nm respectively. Standards containing Cu(II) gave a good linear response (R^2 = 0.9998) and a suitable LOD (0.07 µM), while addition of Fe(III) resulted in excessive absorbance (> 2 AU) in this concentration range, with a poorer linear response (R^2 = 0.9304). Therefore, Cu(II) was selected as the optimum metal for NTA determination and further optimisation was carried out.

Kinetics of the Cu-NTA reaction. In order to identify a suitable protocol for sample and standard analysis, the absorbance at 240 nm was recorded from 0.03 to 10 min (Figure 2.2) after excess Cu(II) (1 mM) was added to a 100 µM NTA aqueous solution. The absorbance was constant after 3 min, suggesting that complexation was complete. The irregular absorbance between 0.3 and 1.5 min after the Cu(II) addition could be due to the multi-step nature of the Cu-NTA complex formation. The fully deprotonated NTA molecule binds to the Cu(II) ion through its oxygen atoms. The Cu-NTA complex forms by successive displacement of water molecules from the $[Cu(H_2O)_6]^{2+}$ by the NTA molecule (Cotton & Wilkinson, 1988). The progressive exchange of water molecules could

transiently change the energy levels of the molecular orbital and, as a consequence, the energy of the electronic transitions between ligand and metal (which are in the UV-visible region). Therefore, standards and samples were left for > 3 min after the addition of Cu(II) prior to measurement.

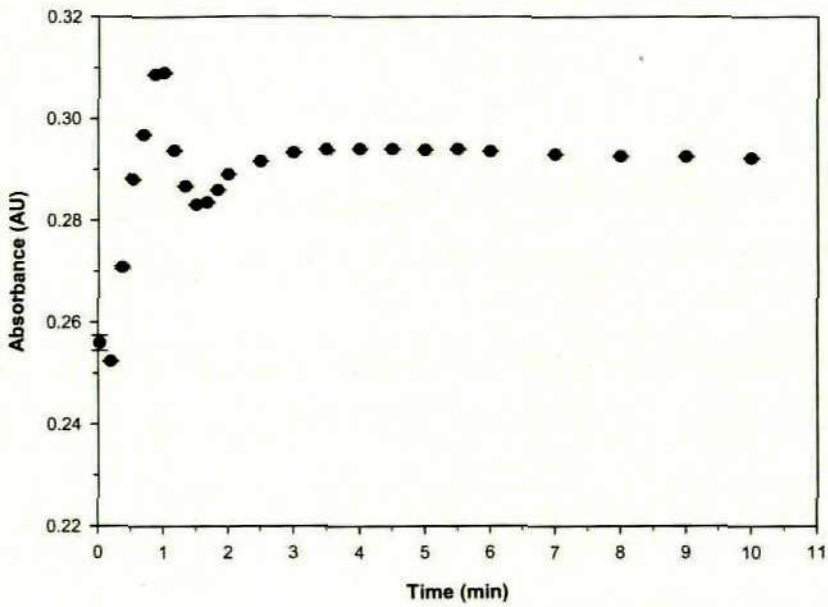

Figure 2. 2 Absorbance over time for the Cu-NTA complex at 240 nm after 1 mM Cu(II) addition to 100 µM NTA aqueous solution. The error bars represent ± one standard deviation of 3 replicate measurements.

Optimisation of the Cu:NTA concentration ratio. NTA complexes copper ions in a 1:1 molar ratio to form $[CuNTA]^-$ (log k = 13.4 ± 0.1; (Norkus & Vaskelis, 1994)). The addition of an equimolar Cu(II) concentration should be sufficient for complete NTA complexation and later UV spectrophotometric detection but it is a good practice to use an excess of the metal to ensure complete complexation. Therefore, to investigate the effect of Cu(II) concentration on NTA complexation, and thus on the absorbance, different Cu:NTA ratios were studied for a 50 µM NTA standard. Solutions containing 1:1, 2:1, 4:1 and 10:1 Cu:NTA ratios were prepared in MilliQ water. A 9 % increase in the absorbance was observed as the ratio increased from 1:1 to 2:1, but no further increase was identified at

ratios > 2:1. Therefore, the method is sufficiently robust for analysis of experimental samples with known initial NTA concentrations. However, as with all methods involving a complexation step, analysis of unknowns requires careful consideration. Other studies have found that between 10 and 33 -fold excess of metal was optimum for the highest standards and the same concentration was used for the unknown samples (Kemmei *et al.*, 2007; Kord *et al.*, 1995; Laamanen *et al.*, 2005a; Laamanen *et al.*, 2005b). For this work, 250 µM was found to be the optimum concentration as it will always provide a molar ratio of Cu(II) to NTA > 2.

The effect of pH on Cu-NTA complexation. To evaluate the effect of pH on Cu-NTA complex formation, four different pHs were investigated for a 100 µM NTA standard with 250 µM Cu(II). The UV absorbance of the unadjusted standard (pH 4.85) was compared with a buffered standard prepared in 0.09 M ammonium acetate (pH 6.80) and with acidic (pH 2.87) and basic (pH 10.57) standards, which were pH-adjusted by the addition of acetic acid and ammonium hydroxide respectively. The speciation diagram for the Cu-NTA system (Figure 2.3, generated with Hydra/MEDUSA speciation modelling software) shows that at 4 < pH < 7, $[CuNTA]^-$ will be the only species in solution. At pH < 4, $[CuNTA]^-$ is still the main species but [CuHNTA] and uncomplexed NTA are also present, while at 9.5 < pH < 11.5 the hydroxide species is predominant. However, experimentally, the pH 2.87 solution did not give a clear absorbance band, suggesting that $[CuNTA]^-$ complex formation was limited and [CuHNTA] does not absorb in the UV region. The buffered (pH 6.80) and pH 10.57 solutions presented a higher background with absorbance at 240 nm > 1 AU. The unadjusted pH solution gave the best response, presenting a clear band and lower absorbance (~0.30 AU) at 240 nm. Since the sand-water mixture has a pH of 7.2 ±

0.2, at which $[CuNTA]^-$ is still the predominant species, no further treatment was needed for optimum NTA determination.

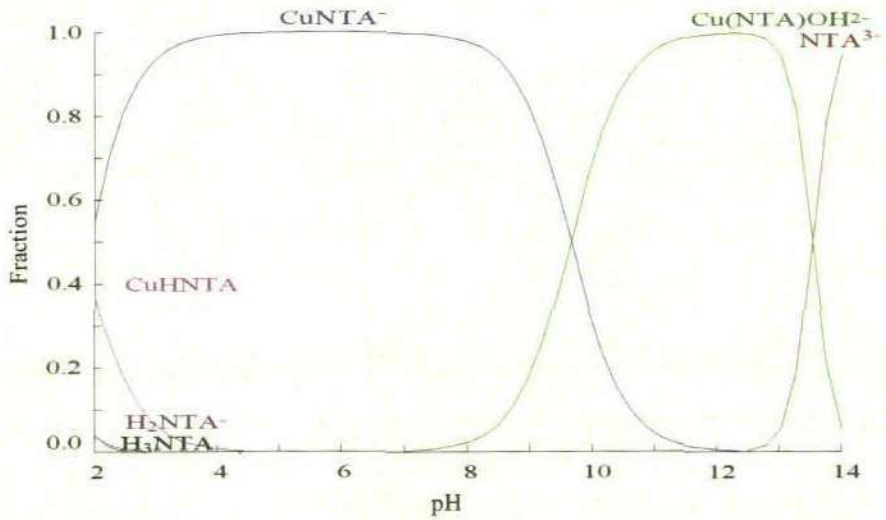

Figure 2. 3 Speciation diagram for a 250 µM Cu(II) and 100 µM NTA system obtained with Hydra/MEDUSA speciation modelling software. Fraction of NTA is shown on the y axis.

Radionuclide competition for NTA. The presence of radionuclides could affect the extent to which the Cu-NTA complex forms through competition for the complexing agents, and thus the absorbance of the complex. The experiments reported in Chapters 3 and 4 used a 5 µM radionuclide concentration; therefore, in order to assess the impact of radionuclide on the Cu-NTA complex response, two sets of five NTA standards (0 – 100 µM) were prepared in MilliQ water and 5 µM of Th(IV) was added to one set. The UV spectra (190 – 350 nm) were recorded at > 3 min after 250 µM Cu(II) addition. Hydra/MEDUSA speciation model predicted that at pH 7.2 and in the presence of excess Cu(II) no Th would be complexed by NTA (log $k_{[ThNTA]}^{+}$ = 15.1) since 100 % of the NTA would be present as the Cu-NTA complex. The calibration graphs with and without Th(IV) (Figure 2.4) were not significantly different (p = 0.062, paired t-test), confirming that 250 µM Cu(II) was able to displace the 5 µM Th(IV) from the NTA complex effectively. The

kinetics of Th(IV) displacement by Cu(II) from the NTA complex were assessed using a 50 μM Th – 100 μM NTA solution in MilliQ water, to which 250 μM Cu(II) was added. Equilibrium was reached after 3 min, suggesting that the reaction is as rapid as the Cu-NTA complexation reaction.

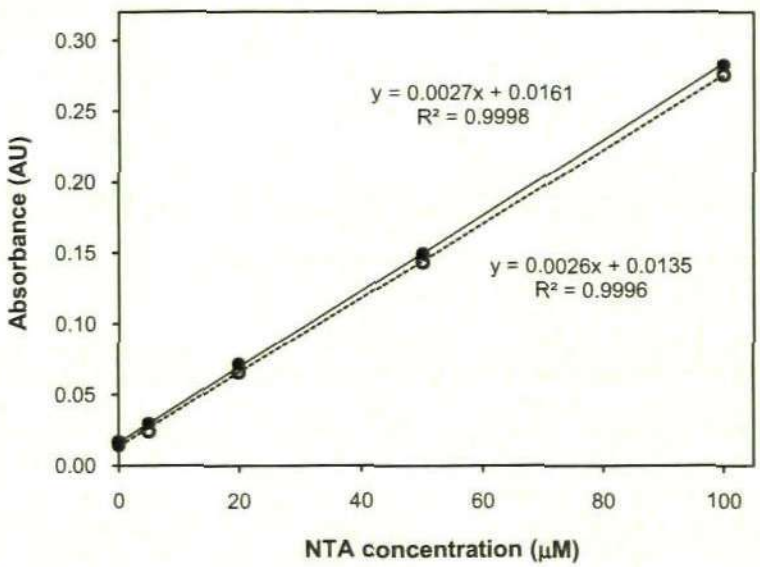

Figure 2. 4 Calibration graphs for NTA standards prepared in MilliQ water with (O) and without (●) 5 μM Th(IV) in solution. Absorbance at 240 nm was recorded at > 3 min after 250 μM Cu(II) addition.

Presence of natural compounds. In order to asses the suitability of the method for use in experiments in Chapters 3 and 4, a sand-water solution was used as the matrix for the preparation of five NTA standards (0 – 100 μM). This allowed the interferences in the UV absorbance spectrum of the Cu-NTA complex from dissolved natural compounds to be assesed. As with picolinic acid, the high sand-water background signal significantly interfered with the signals from all Cu-NTA standards, but when the NTA standards were prepared in 8 % sand-water (diluted with MilliQ), and the diluted sand-water blank (i.e. 0 μM NTA + Cu(II)) was used as the instrumental blank, a good linear response ($R^2 > 0.99$) and LOD < 0.1 μM were obtained. The effect of radionuclides on the kinetics of the

Cu-NTA complexation reaction was also studied in sand-water standards, and the absorbance of the Cu-NTA complex was recorded over 10 min after the Cu(II) addition to a 50 μM Th – 100 μM NTA solution. Equilibrium was again reached after 3 min. Hence, the presence of natural compounds or radionuclides did not affect the Cu-NTA complexation reaction in 8 % sand-water solution.

Optimised conditions. Table 2.3 summarises the optimum conditions for the NTA determination method. The 250 μM Cu(II) provides a molar ratio of Cu(II) to NTA > 2 in both standards (0 – 100 μM) and samples (25 μM is the maximum concentration expected after dilution) analysed within this work. The different optimisation experiments proved that the presence of radionuclides at the concentrations used in Chapters 3 and 4 will not affect the response of the Cu-NTA complex. To obtain representative calibration graphs, standards should be prepared in diluted sand-water (8 %) and the 0 μM standard set as the instrumental blank at the beginning of the analysis to eliminate the background signal from the Cu(II) addition. Figure 2.5 shows the spectra obtained from a set of NTA standards using the optimised conditions. The method has a suitable LOD (0.1 μM) and a linear response ($R^2 > 0.99$) over the range 0 – 100 μM.

Table 2. 3 Optimum conditions for the direct UV spectrometric determination of NTA in sand-water samples.

Complexant metal	Cu(II)
Cu(II) concentration	250 μM
Reaction time	> 3 *min*
pH	no adjustment
λ_{max}	240 nm
Matrix	8 % sand-water

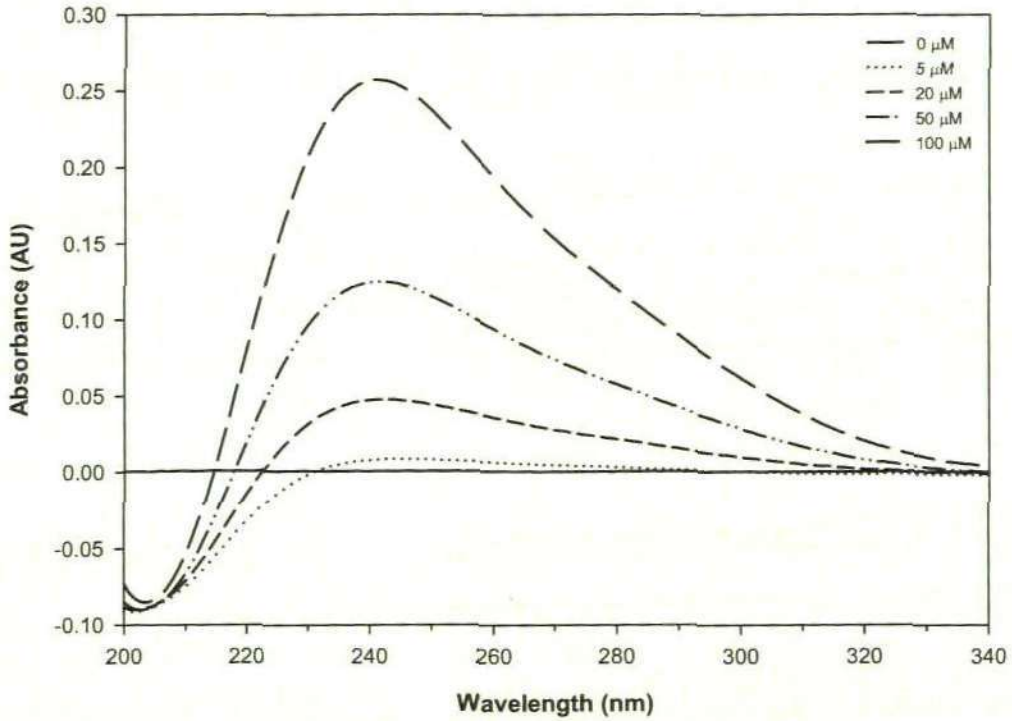

Figure 2. 5 UV spectra obtained with the optimum conditions for NTA standards. The instrumental blank was set using the 0 µM standard.

2.3.3 EDTA determination

EDTA determination by direct UV spectrophotometry following complexation with Cu(II) was investigated but the spectra were noisy and there was a higher absorbance background than for NTA. Therefore, although the response was linear, the LODs were > 0.6 µM. Ion chromatography (IC) with suppressed conductivity detection is a reliable method for EDTA determination in pharmaceutical formulations and canned foods (Krokidis *et al.*, 2005). Metal complexation is not needed and, although a relatively high LOD (2.97 µM) was reported, the linear regression (R^2 > 0.998) and reproducibility (RSD 1.5 %) were good, and the presence of ions commonly dissolved from soils (e.g. chloride) did not affect the resolution of the EDTA peak from other peaks or the sensitivity.

Therefore, as an alternative to the UV spectrophotometry method, IC has been investigated as a possible method for EDTA determination in sand-water solutions.

Selection of mobile phase. EDTA is a weak tetraprotonic carboxylic acid and five species coexist in solution ($[H_4EDTA]$, $[H_3EDTA]^-$, $[H_2EDTA]^{2-}$, $[HEDTA]^{3-}$, $[EDTA]^{4-}$). Their concentration distribution depends on the pH of the mobile phase, and thus the chromatogram can present more than a single peak for EDTA. Krokidis *et al.* (2005) investigated the effect of pH and mobile phase composition on IC separation with conductimetric detection and concluded that the determination of EDTA should be based on a mobile phase with pH < 8.5 (borate buffer) or > 10.5 (carbonate buffer), as $[HEDTA]^{3-}$ and $[NaEDTA]^{3-}$ are the dominant species respectively, and thus a single chromatographic peak for EDTA is obtained. In order to identify the retention time (t_R) for the free anion, a high concentration EDTA standard (2.5 mM) prepared in MilliQ water was analysed using 9 mM carbonate (pH 10.80) as the mobile phase (Table 2.1). A single chromatographic peak at 6.5 min confirmed the presence of the free EDTA anion, most likely to be present as $[NaEDTA]^{3-}$ due to the high Na concentration in the mobile phase (Krokidis *et al.*, 2005).

The concentration of the mobile phase will affect the retention time of the anions, with higher concentrations resulting in shorter retention times. Therefore, mobile phases of 8, 9 and 10 mM carbonate (between pH 10.50 and 10.90) were investigated and resulted in EDTA retention times of 6.86, 6.54 and 6.06 min, respectively. The different mobile phase concentrations did not greatly affect the t_R of the EDTA peak, and since 9 mM carbonate is recommended by Dionex for the determination of inorganic anions (Dionex, 2001), it was selected for further evaluation of the method.

Presence of metal and radionuclide cations. The ability of EDTA to complex metal and radionuclide cations could potentially interfere with the chromatographic separation and determination. To assess the effect of natural metals from the sand-water matrix, five EDTA standards (0 – 100 μM) were prepared in the sand-water mixture and the response was compared with the MilliQ water equivalents. There was no statistical difference (p = 0.563, paired t-test) between the two calibrations. This is supported by Krokidis *et al.* (2005) who found that the presence of Ca^{2+}, Cu^{2+} and Fe^{3+} had no significant effect on the EDTA peak area, since the electronic charge of EDTA species influences their retention on the column but not the detector response. The effect of radionuclide cations was also investigated by the addition of 5 μM Th(IV) to five EDTA standards (0 – 115 μM) in MilliQ water. Again, the response was not significantly different from the MilliQ standards (p = 0.105, paired t-test). In all cases no further peaks were observed and the EDTA retention time did not change.

Separation from natural anions. In order to assess the peak separation of EDTA from common soil anions, equimolar concentrations of chloride, nitrate, phosphate and sulphate were added to five EDTA standards (0 – 250 μM) prepared in MilliQ water. No interferences were observed for these anions with the EDTA peak, which eluted after the chloride peak (Figure 2.6). The chromatographic characteristics calculated from the 250 μM standard chromatogram (Figure 2.6) are shown in Table 2.4. The last species eluted (i.e. sulphate) had a retention factor (k) < 5, confirming a reasonable analysis time. Although baseline resolution (R) between chloride and EDTA and between phosphate and sulphate, was not achieved (R < 1.5), all selectivity factors (α) were > 1 showing that the band centres were successfully separated from each other. The method shows a

well-resolved separation of EDTA from the other anions with a reasonable analysis time; therefore, no modifications from the initial conditions (Table 2.1; (Dionex, 2001)), such as a change of mobile or stationary phase composition, were needed.

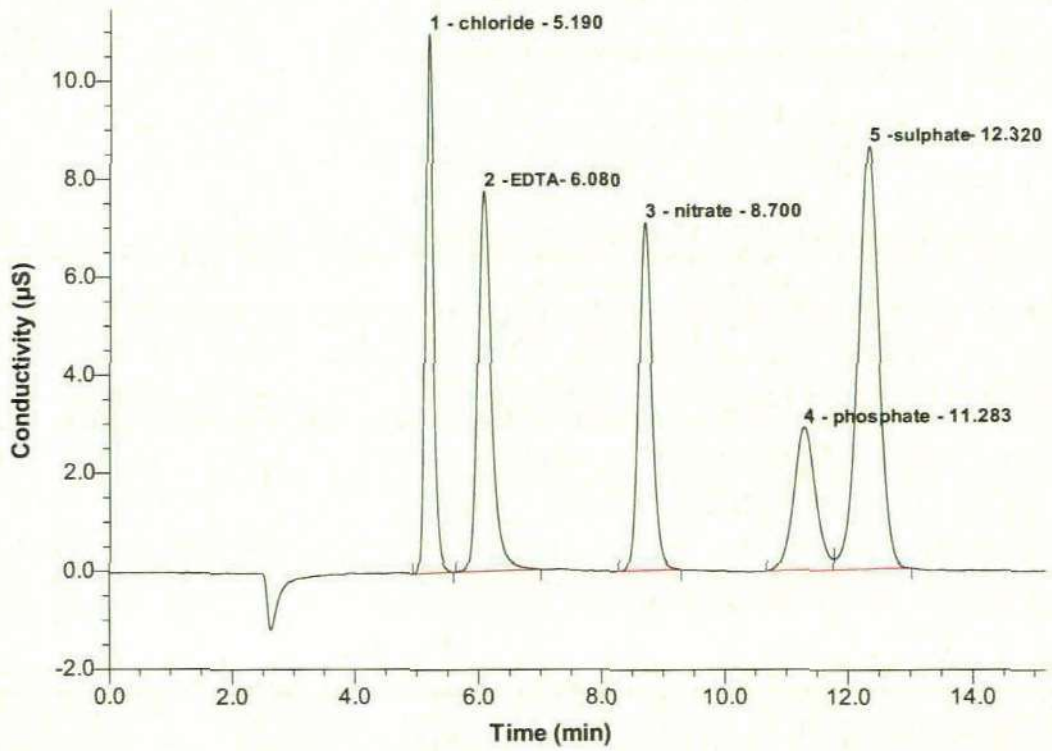

Figure 2. 6 Chromatogram for a 250 µM standard (anions and EDTA) in MilliQ water. Numbers indicate retention time in minutes.

Table 2. 4 Chromatographic characteristics of 250 µM EDTA and anion standard in MilliQ water.

Anion	Retention time (t_R, min)	Peak width (W, min)	Retention factor ($k = (t_R-t_M)/t_M$ = 1-5)	Resolution of adjacent peaks ($R = 2*[t_{RB}-t_{RA}]/W_A+W_B > 1.5$)	Selectivity factor ($\alpha = k_B/k_A > 1$)
Chloride	5.19	0.625	0.99	0.89	1.34
EDTA	6.09	1.375	1.34	2.20	1.74
Nitrate	8.70	1.000	2.34	2.42	1.42
Phosphate	11.28	1.125	3.34	0.83	1.10
Sulphate	12.32	1.250	3.70		

Analytical characteristics for EDTA and anion determination were calculated from a five point calibration graph (0 – 385 µM for anions and 0 – 115 µM for EDTA) in MilliQ water (Table 2.5). All analytes presented a good linear response ($R^2 > 0.99$) and the repeatability was acceptable (RSD < 5 %), except for phosphate (possibly due to the large peak width). The reproducibility between days was also good (RSDs < 5 %) except for EDTA which increased up to 10 % over the 3 days analysed. Nitrate and phosphate had higher LODs than chloride and sulphate, but all were low enough to detect the anions in the sand-water solution. A linear calibration for EDTA over the range 0 – 25 µM was also observed in the undiluted sand-water mixture ($R^2 = 0.9983$) and the gradient (0.0062 AU μM^{-1}) showed no significant difference compared with MilliQ water standards. Since the EDTA separation and response were not affected by the sand-water mixture, samples containing EDTA do not require dilution prior to analysis. Moreover, the addition of several major anions to the EDTA standards permitted their determination in the sand-water solution (the concentrations found were 0.23 ± 0.01, 4.02 ± 0.14 and 0.13 ± 0.01 mM of chloride, nitrate and sulphate respectively).

Table 2. 5 Analytical characteristics of EDTA and inorganic ion determination for a 5 point calibration (0 – 385 µM) in MilliQ water.

Anion	*Blank* (µM)	*Gradient* (AU μM^{-1})	*Intercept* (AU)	R^2	*% RSD* ** (3 injections)	*% RSD* ** (3 days)	*LOD* (µM)
Chloride	4.60 ± 0.18	0.0066	-0.0279	0.9991	1.3	1.4	0.54
*EDTA**	0.70 ± 0.09	0.0066	-0.0028	0.9978	4.6	10.1	0.27
Nitrate	5.73 ± 1.30	0.0064	-0.0251	0.9989	0.8	2.7	3.91
Phosphate	6.40 ± 1.77	0.0027	-0.0116	0.9982	6.3	4.6	5.31
Sulphate	2.23 ± 0.03	0.0132	-0.0280	0.9996	1.1	2.7	0.08

*EDTA calibration from 0 – 115 µM; **calculated for the 45 µM standard

2.3.4 Determination of EDTA, NTA and picolinic acid sorption to solid phases

In order to assess the capability of the methods for determining the sorption of EDTA, NTA and picolinic acid to sand, triplicate samples were prepared using 10 mL of a MilliQ solution containing 200 µM EDTA, NTA or picolinic acid, with and without 5 g solid phase (natural sand or silica). The samples were mixed in an orbital shaker for 168 h, and then sub-samples were taken for EDTA, NTA and picolinic acid determinations using the optimised UV and IC methods described in this chapter. The results obtained are shown in Table 2.6. The concentration measured for the samples with no solid phase agreed with the initial concentration added, suggesting that there was negligible sorption to the walls of the vessels after 168 h. However, samples containing sand or silica showed some level of sorption to the solid phase, especially for picolinic acid which was almost completely removed from solution. The relatively low % RSDs for 3 replicate samples (2 – 5 % for EDTA, 2 – 7 % for NTA, 4 – 8 % for picolinic acid) confirmed the acceptable reproducibility of the methods and their capability to determine the 3 organic complexing agents in the later experiments described in Chapters 3 and 4.

Table 2. 6 Concentrations determined and recoveries in 200 µM organic complexing agent standards with and without 5 g solid phase after a 168 h incubation time. The uncertainties represent ± one standard deviation of three replicate samples.

Organic complexing agent added (200 µM)	Concentration detected (µM)			Recovery (%)*
	No solid phase	*Sand*	*Silica*	
EDTA	199 ± 5	180 ± 3	161 ± 8	99 ± 2
NTA	201 ± 14	200 ± 4	199 ± 9	100 ± 7
Picolinic acid	198 ± 17	4.2 ± 0.3	43 ± 2	99 ± 8

*for the samples without solid phase

2.4 Conclusions

Direct UV determination at 265 nm is a simple and quick method for picolinic acid determination, which was not affected by the presence of Th. NTA determination involved an extra step with Cu(II) complexation, but the short time needed to achieve quantitative Cu-NTA complex formation (3 min) did not increase the analysis time significantly. The addition of excess Cu(II) displaced other metals and/or radionuclides from any other complexes formed, and the approach is appropriate for a wide range of soil waters without pH adjustment. To reduce the effect of the DOC background and obtain representative calibration graphs, picolinic acid and NTA standards were prepared in diluted sand-water. Samples require the same dilution as the standards, which clearly lowers the concentration of complexing agent available for analysis, but the low LOD obtained for both organic complexing agents (< 0.15 μM), allowed the determination of picolinic acid and NTA concentrations used throughout this work (5 – 200 μM or 0.4 – 16 μM after dilution). Ion chromatography with suppressed conductivity detection provided an acceptable LOD for EDTA determination in sand-water solutions (0.3 μM). This technique required a longer analysis time (still < 15 min per injection) but had the advantages of not needing sample pre-treatment (i.e. neither metal complexation nor sample dilution) and the ability to quantify the major inorganic anions. The optimised methods for the specific determination of picolinic acid, NTA and EDTA in the sand-water mixtures have the necessary analytical figures of merit to be applied to the main radionuclide sorption experiments described in Chapters 3 and 4 with no significant interferences from natural cations or anions (originating from the solid matrix) or from spiked radionuclides.

Chapter 3

Characterising the interactions between Th, organic complexing agents and natural sand

3.1 Introduction

Anthropogenic organic ligands used during nuclear plant decontamination and waste reprocessing (such as EDTA, NTA or picolinic acid) form stable aqueous complexes with radionuclides and metals and hence may increase their mobility through the environment. However, studies on a range of radionuclides and metals in diverse environments have shown contrasting results. For example, EDTA has been found to actively promote UO_2^{2+} migration through intact sandstone cores (Read *et al.*, 1998). However, Serne *et al.* (2002) observed no change in U(VI) and Th(IV) sorption to a synthetic Fe-coated sand, or to a natural sandy soil, in the presence of equimolar EDTA (10^{-5} M), reflecting a lack of significant radionuclide-ligand complex formation. Nonetheless, the formation of the EDTA complex prevented the sorption of Pb(II) onto SiO_2 (Bowers & Huang, 1987). These contrasting observations demonstrate the effect of system characteristics on radionuclide complexation and highlight the need to explore the mechanisms by which co-disposed organic complexing agents can affect the solubility of radionuclides.

The aim of the work described in this chapter was therefore to study the effect of different organic complexing agents on radionuclide solubility in the presence of a natural solid phase and elucidate the interaction mechanisms. The species selected for this work were Th, as a representative actinide(IV), three organic complexing agents with different *denticities (EDTA, NTA and picolinic acid) as common co-contaminants present in nuclear* waste, and two solid phases (pure silica as an artificial solid phase and dune sand as a simple natural solid phase). In order to deduce the mechanisms controlling the interactions in the system (Figure 3.1), the following processes were quantified: i) the

sorption kinetics of Th to the solid phases, using inductively coupled plasma-mass spectrometry (ICP-MS); ii) complexing agent sorption to the solid phase using ion chromatography (IC) and UV spectrometry; iii) metal desorption from the solid phase using inductively coupled plasma-optical emission spectrometry (ICP-OES). Finally, solution phase speciation was studied qualitatively using electrospray ionisation-mass spectrometry (ESI-MS).

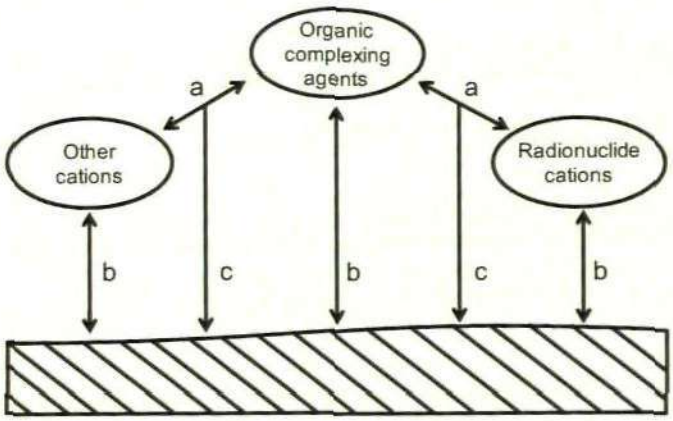

Figure 3. 1 Possible interactions between radionuclides, organic complexing agents and a solid phase: a) cation complexation in the solution phase; b) sorption of uncomplexed cations and complexing agents to the solid phase; and c) sorption of complexed cations to the solid phase.

3.2 Experimental

3.2.1 General

All plasticware used in these experiments was soaked in 2 % v/v Decon overnight, rinsed with MilliQ water (Millipore, 18.2 MΩ cm^{-1}), soaked in 10 % m/v HCl overnight, rinsed with MilliQ water again, air dried and stored in double zip lock plastic bags to avoid contamination. All chemicals used in these experiments were analytical grade and all

solutions and experiments described in this chapter were prepared using MilliQ water and carried out in an ISO 9001:2000 accredited laboratory.

3.2.2 Thorium, organic complexing agents and solid phases

Thorium was obtained as the nitrate salt from BDH Chemicals Ltd (Poole, England) and solutions were prepared in a designated laboratory for radioisotope use. The nitrate salt was added to a pre-weighed vessel inside a fume hood over a work tray, sealed, weighed outside the fume hood on a four-figure balance (Salter Electronic Balance ER-182A), and then the salt was dissolved to make the relevant stock solutions inside of the fume hood. EDTA sodium salt was obtained from Fisher Scientific (Loughborough, UK) and NTA sodium salt and picolinic acid were obtained from Sigma-Aldrich (Gillingham, Dorset, UK).

Dune sand from Drigg Sands in Cumbria (UK) was chosen because of its proximity to the low-level waste (LLW) repository managed by the British Nuclear Group. The sand was sieved to < 2 mm using a plastic sieve (nylon) to remove organic debris and large grains and stored in a plastic container at room temperature until use. Silicon dioxide crystalline (fine), coating quality, ≥ 99.9 %, 200 - 700 µm particle size, was obtained from Sigma-Aldrich (Dorset, UK).

3.2.3 Experimental design

All batch sorption experiments were prepared in 50 mL plastic centrifuge tubes (Western Laboratory Service, Hampshire, UK). In all experiments, 5 g of solid phase was weighed using a four-figure balance and the stock solutions were mixed and added to the sand to give a final Th concentration of 5 µM with the desired concentrations of organic

complexing agent in 10 mL of solution. Two approaches were taken; the standard approach involved adding the aliquots of the stock solutions directly to the sand, and the alternative approach involved pre-equilibrating the solution for 24 h. Cartwright *et al.* (2007) found that 24 h was sufficient time for Th-EDTA and Th-NTA complexes to form. Procedural blanks and experiments without sand were also prepared to assess contamination and sorption to the walls of the vessel, respectively. All experiments were carried out in triplicate using an orbital shaker (KS125 basic, JK Ika Labortechnink). After the required incubation time, the centrifuge tubes were transferred to a centrifuge (Legend RT Centrifuge) and centrifuged at 3500 rpm for 6 min (980 *g* centrifugal force). Aliquots of the supernatant were diluted and acidified with 2 % HNO_3 for ICP-MS and IPC-OES analyses. Diluted aliquots (with MilliQ) were used for UV spectrometry, and undiluted supernatant was taken for IC and ESI-MS analysis. To investigate sorption kinetics, 100 µL sub-samples were taken over time so that a maximum of 1 % of the solution was removed at each time point in any given experiment.

Degradation of the complexing agents over time was investigated in MilliQ water that had been equilibrated with sand in a 5 g : 10 mL solid : solution ratio for 24 h. The mixtures were then centrifuged (3500 rpm for 6 min) and the supernatant transferred to a clean centrifuge tube. This sand-water was then spiked in triplicate with organic complexing agents to give a range of concentrations between 5 ~ 200 µM, and sub-samples were taken over time up to 672 h.

Table 3.1 summarises the conditions of the experiments under which radionuclide sorption and the effect of organic complexing agents were studied. Seven days (168 h)

was selected for many experiments as a practically achievable length of time which allowed the systems to approach equilibrium, (see section 3.3.2 for further details).

Table 3. 1 Experimental conditions for the sorption experiments. OCA = organic complexing agent.

System	Effect studied	Solid phase (g)	Th (μM)	OCA (μM)	Incubation time (h)
Sand/Th	Sorption kinetics	5	5	-	From 0.5 to 702
Silica/Th	Sorption	5	5	-	168
Sand/OCA	Sorption kinetics	5	-	5, 20, 80, 200	From 1.5 to 672
Sand-water/OCA	Degradation	-	-	20, 200	From 1.5 to 672
Silica/OCA	Sorption	5	-	5, 200	168
Sand/Th/OCA	Sorption kinetics	5	5	500	From 0.5 to 702
	Effect of OCA concentration on Th sorption	5	5	5, 20, 80, 200	24 and 168
	Effect of solution pre-equilibration (24 h) on Th sorption	5	5	5, 20, 80, 200	24 and 168
	Effect of OCA on matrix metal desorption	5	5	5, 20, 80, 200	From 24 to 672
Silica/Th/OCA	Effect of OCA concentration on Th sorption	5	5	5, 200	168
	Effect of OCA on matrix metal desorption	5	5	5, 200	168

3.2.4 Analytical methodology

Solid phase characterisation. The particle size distribution of the 2 mm sieved sand was obtained by a laser diffraction method (Malvern Long-bed Mastersizer X with wet sample unit MS17, Malvern Instruments Ltd, UK) following digestion of the organic content with 30 % hydrogen peroxide. The N_2-BET specific surface area was obtained using a Gemini

2375 V4.01 Instrument (Micromeritics) and the total carbon, hydrogen and nitrogen (CHN) content was determined using a gas chromatography technique (EA 1110 CHN Analyser), in which the soil is completely combusted and the gases produced are analysed by chromatography with thermal conductivity detection. The cation exchange capacity (in mEq per 100 g of dry soil) was determined through exchange with sodium following the US Environmental Protection Agency (EPA) SW-846 Method 90812 (EPA, 1986). The sodium concentration was measured using a flame photometer (Corning 400 Falem Photometer), calibrated with sodium chloride standards. The soluble organic components of the sand were quantified by dissolved organic carbon (DOC) analysis using a TOC-5000A analyser coupled with an ASI 5000A autosampler calibrated with potassium hydrogen phthalate ($C_6H_4(COOK)(COOH)$) standards. Selected sand particles were examined by electron microscopy (JSM-6100 Scanning Microscope A) with Energy Dispersive X-Ray analysis (EDAX) to obtain a qualitative assessment of the mineralogical composition of the sand. Finally, the pH of the experimental soil solutions was measured using a conventional pH meter (Mettler Delta 340).

Thorium and matrix metal determinations. The acidified sub-samples from the experiments were stored at 4 °C until the day of the analysis. Thorium was determined by ICP-MS (VG Plasmaquad PQ2+Turbo, Winsford, Cheshire, UK) while dissolved metals were determined by ICP-OES (Varian 725-Es, ICP-OES Instrument, Varian, Yarton, Oxfordshire, UK). The standards for both ICP-MS and ICP-OES calibration graphs were prepared from plasma emission standards (Aristar, 10,000 μg mL^{-1} for Sr, Fe, Ca, K, Mg, Zn and Mn; Alfa Aesar, 1,000 μg mL^{-1} for Th). Prior to ICP-MS analysis, 50 μg L^{-1} of ^{115}In and ^{209}Bi were added as internal standards to all samples, blanks and working standards. During both

ICP-MS and ICP-OES analyses, instrumental drift was assessed by measuring calibration series at the beginning, middle and end of the analytical sequence, and a blank and standard were measured after every 12-15 samples. The LOD (as defined in section 2.3.1) was always < 1 nM for Th and < 0.8 μM for dissolved metals (except for K which LOD was ~ 30 μM).

EDTA, NTA and picolinic acid determinations. Aliquots of the supernatant were diluted with MilliQ water, stored at 4 °C and analysed within 2 days. EDTA was determined by ion chromatography and NTA and picolinic acid by UV spectrophotometry, following the methods developed and described in Chapter 2.

Qualitative complex determination using ESI-MS. Aliquots were taken directly from the silica experiments and analysed by ESI-MS. A manual flow injection system was used (5 μL sample loop metal-free Rheodyne injector, model number 9125, CA, USA) with a Chromasoln Plus HPLC water carrier at a flow rate of 150 μL min^{-1} (P580 binary pump, Dionex Softron GmbH, Germering, Germany). Chromasolv Plus HPLC methanol (Sigma-Aldrich) was used to clean the system before and after analyses. Mass spectrometry analysis was performed using an ion trap mass spectrometer fitted with an electrospray interface (ThermoQuest Finnigan Mat LCQ, San Jose, CA). Data were acquired and processed with Xcalibur 1.0 software. Mass spectra were recorded in the negative and positive ion mode between *m/z* 50-2000. All analyses were performed in triplicate.

Speciation modelling. The aqueous geochemical speciation of Th was modelled using Visual MINTEQ, ver. 3.0, beta software. The calculations were based on the aqueous

stability constants of the complexing agents with Th and common matrix metals. Solid phase interactions were excluded. The calculations were performed with the organic complexing agent and Th concentrations added and the measured experimental pH and cation concentrations.

3.3 Results and discussion

3.3.1 *Natural sand and silica characterisation*

Ninety one % of the natural sand particles were between 175 and 707 µm and only 0.08 % was classified as silt (32 – 63 µm). The N_2-BET surface area for the sand was 0.1193 $m^2 g^{-1}$, a low value consistent with the particle size distribution, and the sodium cation exchange capacity was 0.89 ± 0.12 mEq / 100 g. The total C content of the sand was 0.29 ± 0.02 %, of which 0.14 ± 0.02 % was organic carbon, and N and H were below the limit of detection. The dissolved organic carbon concentration was 1.28 ± 0.32 mM C after 168 h, which is *equivalent to ~ 15.5 mg C* L^{-1}. *This DOC concentration falls within the range associated* with sandy soils of 0 – 30 mg C L^{-1} (Kalbitz *et al.*, 2000) and is consistent with the low organic C concentration of the sand. EDAX analysis indicated that > 85 % of the sand surface was silica (SiO_2) with smaller percentages of Al_2O_3, K_2O, CaO, Fe_2O_3, TiO_2, Na_2O, MgO and MnO. This qualitative composition compared well with a previous quantitative XRF analysis of the same sand (Handley-Sidhu, 2006). The dissolution of inorganic ions from the sand resulted in constant concentrations of 0.23 ± 0.01, 4.02 ± 0.14 and 0.13 ± 0.01 mM chloride, nitrate and sulphate respectively. The sand had a pH buffering capacity producing a consistent experimental pH of 7.2 ± 0.2 after 24 h.

The silica was defined by the supplier as 200 – 700 μm, with a purity ≥ 99.9 %. The concentrations of dissolved organic carbon and inorganic ions dissolved from the silica surface were below the limit of detection. The silica buffered all experimental solutions to pH 6.9 ± 0.3. Therefore the sand and silica used were of similar size and generated experimental pH values that were within uncertainty of one other.

3.3.2 Effect of organic complexing agents on Th sorption

Th sorption to silica and complexing agent effect. The effect of a 40-fold excess of ligand (200 μM) on Th (5 μM) sorption to silica was determined after 168 h (7 d). Figure 3.2 shows that, in the absence of the ligand, Th had a high affinity for the silica, with 98.9 ± 0.1 % sorbed after 168 h. The presence of EDTA and NTA resulted in 101 ± 5 and 101 ± 6 % of the Th remaining in solution respectively, which is consistent with the high stability constants of these complexes (Table 3.2). Picolinic acid had a much smaller effect on Th solubility, increasing the concentration of Th in solution 4-fold. The solubilisation of Th by EDTA and NTA in this system shows that the complexes are soluble and stable in the presence of the fairly weak binding sites on the silica surface. The lower denticity of picolinic acid is consistent with the more limited effect on Th solubility, but there are no reported stability constants for Th-picolinate.

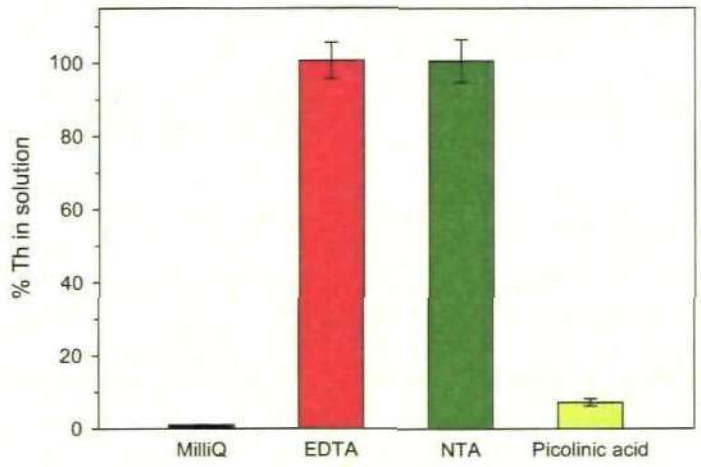

Figure 3. 2 Thorium (5 µM) sorption to silica with and without a 40-fold excess of organic complexing agent. The % Th remaining in solution after 168 h is shown for the silica systems with MilliQ water (■) and in the presence of 200 µM EDTA (■), NTA (■) and picolinic acid (■). The error bars represent ± one standard deviation of three replicate samples.

Table 3. 2 Stability constants (log *k*) for EDTA, NTA and picolinic acid and Th and common metal cations. Data obtained from Cartwright *et al.* (2007), Serne *et al.* (2002) and Stumm & Morgan (1996).

Cation	EDTA		NTA		Picolinic acid	
	Species	***Log k***	***Species***	***Log k***	***Species***	***Log k***
H^+	HL^{3-}	11.12 / 11.0	HL^{3-}	10.33	HL	5.39
	H_2L^{2-}	17.8 / 17.3	H_2L^{2-}	13.27	H_2L^+	6.40
	H_3L^-	21.04 / 19.6	H_3L^-	14.92		
	H_4L	23.46 / 21.8	H_4L	16.02		
	H_5L^+	24.76				
Th^{4+}	ThL	26.8	ThL^+	15.1 / 19.5		
	$ThHL^+$	28.8	ThOHL	6.49		
	$ThOHL^-$	19.5				
Ca^{2+}	CaL	12.4 / 11.0	CaL	7.6	CaL^+	2.2
	$CaHL^-$	16.0			CaL_2	3.8
Fe^{3+}	FeL^-	27.7	FeL	17.9	FeL_2^+	13.9
	FeHL	29.2	FeL_2	26.3	$FeOHL_2$	24.9
	$FeOHL^-$	33.8 / 19.8				
	$Fe(OH)_2L^{2-}$	37.7 / 9.7				
K^+	KL^{3-}	1.7				
Mg^{2+}	MgL	10.6 / 8.95	MgL	6.5	MgL^+	2.6
	MgHL	15.1			MgL_2	4.0
Mn^{2+}	MnL^{2-}	15.6	MnL	8.7	MnL^+	4.0
	$MnHL^-$	19.1	MnL_2	11.6	MnL_2	7.1
					MnL_3^-	8.8
Zn^{2+}	ZnL^{2-}	18.3	ZnL	12.0	ZnL^+	5.7
	$ZnHL^-$	21.7	ZnL_2	14.9	ZnL_2	10.3
	$ZnOHL^{3-}$	19.9	ZnOHL	15.5	ZnL_3^-	13.6

Sorption kinetics and the effect of excess complexing agent on Th sorption to natural sand. When the complexity of the solid phase was increased by using a natural sand, the organic ligands had a very different effect on the sorption behaviour of Th (Figure 3.3). In the absence of the ligands, sorption was slow and followed a broadly linear trend (R^2 > 0.98; ~ 30 % sorbed after 24 h). The addition of 100-fold excess NTA or picolinic acid slightly enhanced the rate of Th sorption (p = 0.012 and 0.027 respectively, paired t-test) and the presence of 100-fold excess EDTA resulted in significantly more rapid Th removal from solution (p < 0.001, paired t-test). Thorium sorption was at equilibrium after 552 h (23 d) when no complexing agent was present, while sorption reached equilibrium between 144 and 168 h in the presence of the complexing agents. Therefore, in this natural sand system, the complexing agents increased the rate of Th sorption but did not affect the equilibrium distribution.

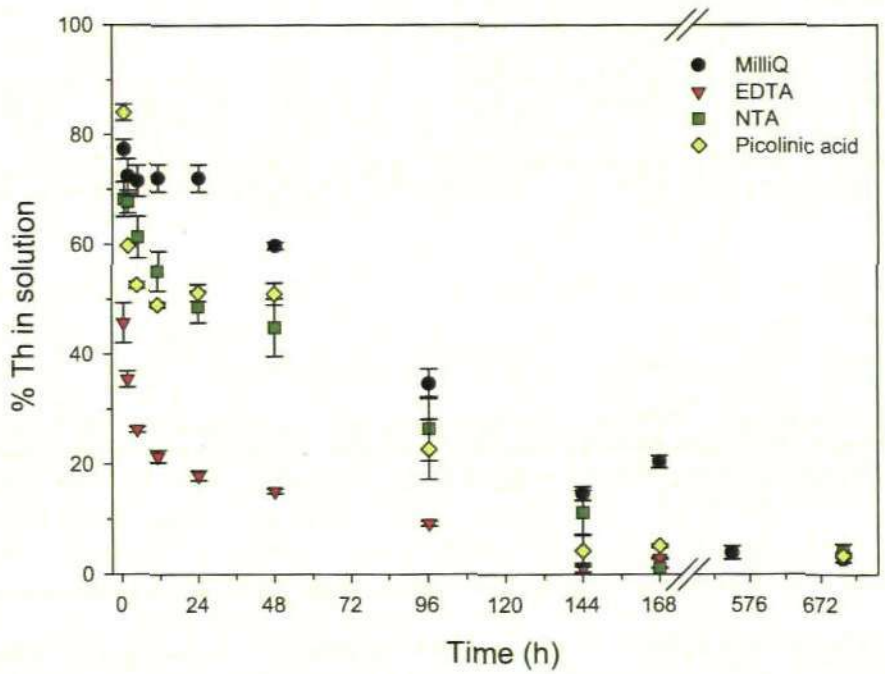

Figure 3. 3 Effect of organic complexing agents on the sorption kinetics of 5 µM Th. The % Th remaining in solution is plotted against time (h) for the experiments containing solutions of MilliQ water (●), 500 µM EDTA (▼), 500 µM NTA (■) and 500 µM picolinic acid (●). The error bars represent ± one standard deviation of three replicate samples.

Effect of complexing agent concentration and solution pre-equilibration on the rate of Th sorption. A 24 h incubation time was used to assess the effect of complexing agent concentration and the pre-equilibration of Th with the complexing agents on the kinetics of Th sorption. Figure 3.4 A shows that without pre-equilibration equimolar EDTA (5 μM) enhanced Th sorption from 28 to 63 % in this time period and a 4-fold excess of EDTA (20 μM) increased this to 89 %. Higher EDTA concentrations (80 and 200 μM) had no further effect. However, pre-equilibration of the Th-EDTA solution (24 h) had a significant effect on Th sorption in this time period for all EDTA concentrations and, with 20 - 200 μM EDTA, the system reached equilibrium (96 % Th sorption).

Increased NTA concentrations increased the rate of Th sorption across the range investigated (Figure 3.4 B). Again, this was enhanced by pre-equilibration of the Th-NTA solution, thus the pre-equilibrated 40-fold excess NTA system reached sorption equilibrium within 24 h. Picolinic acid affected Th sorption to a lesser extent than NTA or EDTA thus sorption equilibrium was not reached in the 24 hour period even with the highest ligand concentration (Figure 3.4 C). However, the rate of Th sorption was increased significantly with higher ligand concentrations and following pre-equilibration of the complexes.

The general trends of faster Th sorption with greater ligand concentrations and with pre-equilibration strongly suggest that the rate is a function of the speciation of Th, with complexed Th sorbing more rapidly than "free" Th species.

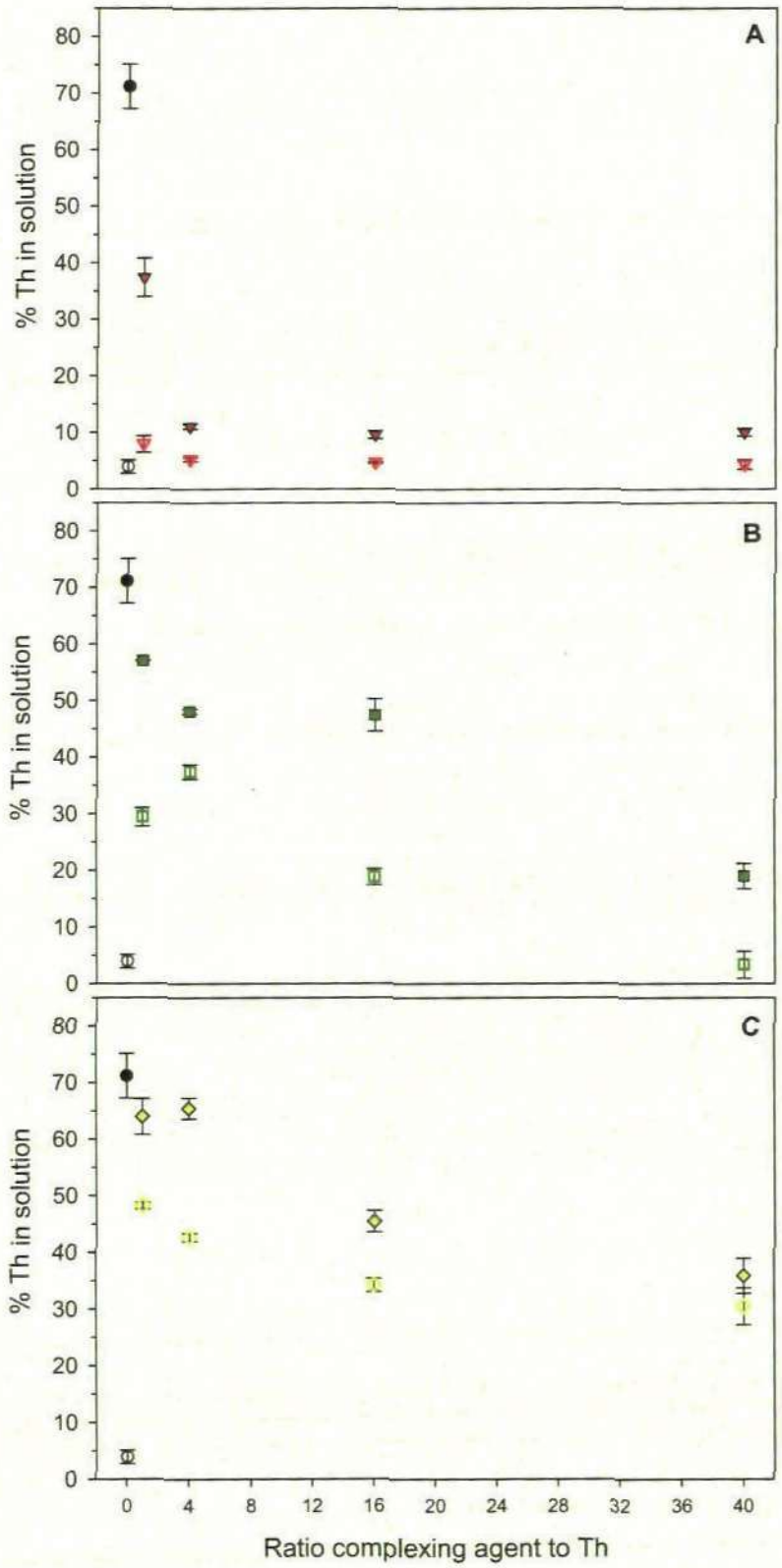

Figure 3. 4 Effect of organic complexing agent concentration and solution pre-equilibration on Th (5 µM) sorption after 24 h incubation time. The % Th remaining in solution is plotted against molar ratio of complexing agent to Th for experiments with solutions containing MilliQ at 24 h (●) and at sorption *equilibrium (○, 552 h), and for not pre-equilibrated (filled symbols -* ▼, ■, ◆*) and pre-equilibrated (open* symbols - ▽, □, ◇) experiments containing solutions of **A**) EDTA, **B**) NTA and **C**) picolinic acid at 24 h. The error bars represent ± one standard deviation of three replicate samples.

3.3.3 Characterising changes in the solution phase

Complexing agent degradation and sorption to silica and natural sand. EDTA and NTA do not occur naturally in the environment but when present due to anthropogenic inputs they can be used as an energy source by soil microorganisms (Bucheli-Witschel & Egli, 2001). Picolinic acid is a naturally occurring degradation product of tryptophan (an essential amino acid) but it is not abundant in natural organic matter samples (Coughlin & Stone, 1995). However, there are pyridine derivatives that are bacterially degraded (Fetzner, 1998), suggesting that picolinic acid could be used by organisms in soils. Here, no degradation of the complexing agents was observed in the sand-water solutions over 168 h (7 d). This is consistent with both the slow degradation rate of EDTA and NTA identified by Means *et al.* (1980) under ideal laboratory conditions, and with their environmental persistence.

Complexing agent sorption to the silica and sand was studied in the 168 and 672 h incubation experiments (7 and 28 days) respectively. Figure 3.5 shows the sorption of organic complexing agents to sand in the experiments containing 200 μM EDTA, NTA or picolinic acid solutions. In the sand system, a maximum of 20 % of the EDTA sorbed over the 672 h experiment. In the presence of silica, similar sorption was observed, with 18 % of the EDTA removed from solution after 168 h. For NTA, < 5 % sorbed to the sand or silica during the experimental time period. These sorption values are consistent with the relatively low affinities of the complexing agents for soils reported in the literature, e.g. Maset *et al.* (2006) found that EDTA was not significantly sorbed to a silty loam soil; Serne *et al.* (2002) found that about 10 % EDTA sorbed to a low iron sandy soil; and Means *et al.* (1980) found that NTA was not degraded or sorbed to an aquifer soil at pH 7.4. In the case

of picolinic acid, sorption to the sand was broadly linear (R^2 > 0.96) with > 95 % of the picolinic acid removed from solution after 336 h. In the silica system, sorption was slightly lower, with about 75 % sorbed after 168 h. Significant sorption of picolinic acid has also been observed onto a synthetic Fe-coated sand and to a natural sandy soil, pH 6-7 (Serne *et al.*, 2002). This affinity for the sand matrix may result from the ability of the ligand to bind to the solid surface via its amine or carboxylate functional groups (Davis & Leckie, 1978).

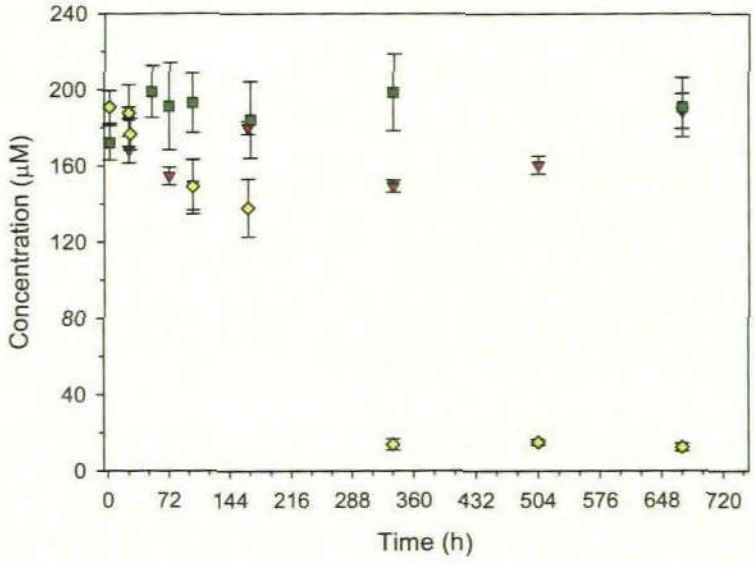

Figure 3. 5 Sorption of organic complexing agents to sand. EDTA, NTA and picolinic acid concentration remaining from a 200 µM EDTA (▼), 200 µM NTA (■) and 200 µM picolinic acid (●) solutions plotted against time. The error bars represent ± one standard deviation of three replicate samples.

Similar percentages of the complexing agents were sorbed when they were present at a 5 µM concentration with 5 µM Th. Fourteen percent of the EDTA and > 95 % of the picolinic acid sorbed to the sand over 168 h, and 0 % of the EDTA and NTA and 60 % of the picolinic acid sorbed to the silica. Data for NTA sorption to sand are not available. These data confirm that sorption of EDTA was not significant in any of the experiments, and importantly, that Th was not sorbed as a surface bound Th-EDTA complex.

Cation desorption from silica and natural sand surfaces. Low metal concentrations desorbed from the pure silica surface into MilliQ water or solutions of the ligands (Table 3.3). Maximum desorption was seen with 200 μM EDTA, with 41 μM Fe and a small increase in the Mn concentration (2 μM). The presence of NTA and picolinic acid brought less Mn and Fe into solution, which is consistent with the reported stability constants of these complexes (see Table 3.2).

Table 3. 3 Metal cation concentrations desorbed into solution from silica (5 g) after 168 h in the presence of 200 μM concentration of organic complexing agents. Blank values (MilliQ experiments) have been subtracted and where no data are shown no significant changes were detected. The uncertainties represent *± one standard deviation of three replicate samples.*

Metal cations desorbed	***Silica system***			
	MilliQ	***+ EDTA***	***+ NTA***	***+ picolinic acid***
Ca	19 ± 1			
Fe	0.5 ± 0.1	41 ± 2	7.2 ± 0.2	4.5 ± 0.1
K	99 ± 7			
Mg	12.0 ± 0.2			
Mn	0.6 ± 0.1	1.9 ± 0.1	0.2 ± 0.1	0.5 ± 0.2
Zn	0.3 ± 0.1			
Total (μM)	–	42 ± 2	7.4 ± 0.2	5.0 ± 0.2

Metal desorption from the sand surface was studied from 24 to 672 h, and there was a high initial desorption of Ca, Mg and K (1355, 251 and 322 μM respectively) into MilliQ water after 24 h. Figure 3.6 shows that the Ca concentration increased linearly from 24 to 168 h ($R^2 > 0.98$) and then reached a plateau. EDTA enhanced the concentration of Ca that desorbed in the first 24 h, and the subsequent changes in concentration followed the same pattern as desorption into MilliQ water, offset by 262 ± 63 μM Ca on average over

the time period. In contrast, the presence of the organic complexing agents did not significantly affect the Mg and K concentrations compared with the MilliQ system (all systems with $p > 0.10$) and after the initial input the concentrations did not change. The presence of EDTA also enhanced Zn desorption, with 3.6 ± 0.5 μM Zn solubilised in the first 24 h. This is a similar concentration to the additional Th lost from solution in this time period due to EDTA, of 2.5 ± 0.1 μM. Solubilisation of Zn then continued, in a broadly inverse pattern to Th sorption, reaching a plateau at 348 h. The Fe and Mn concentrations in solution were also affected by the presence of EDTA. However, the Fe concentration only increased significantly after 168 h and although Mn had an initial input of 6.9 ± 0.8 μM during the first 24 h, its concentration then decreased linearly ($R^2 = 0.99$) to below the limit of detection after 168 h.

NTA had no effect on Ca desorption but also resulted in the desorption of 1.8 ± 0.1 μM Zn into solution in the first 24 h, which corresponds to the period of enhanced Th sorption, when an additional 0.9 ± 0.2 μM Th sorbed over the MilliQ system. There was no further release of Zn into solution after 24 h. The picolinic acid system showed a comparable rate of Th sorption to the NTA system, however, the cation desorption profile was very different with no significant Zn release and a similar overall solubilisation of Ca over the time period to EDTA (179 ± 61 μM Ca, $p = 0.075$). Overall, the cation data suggest metal exchange occurs at the sand surface in the presence of the EDTA and NTA, with Th exchanging with Zn and/or Ca.

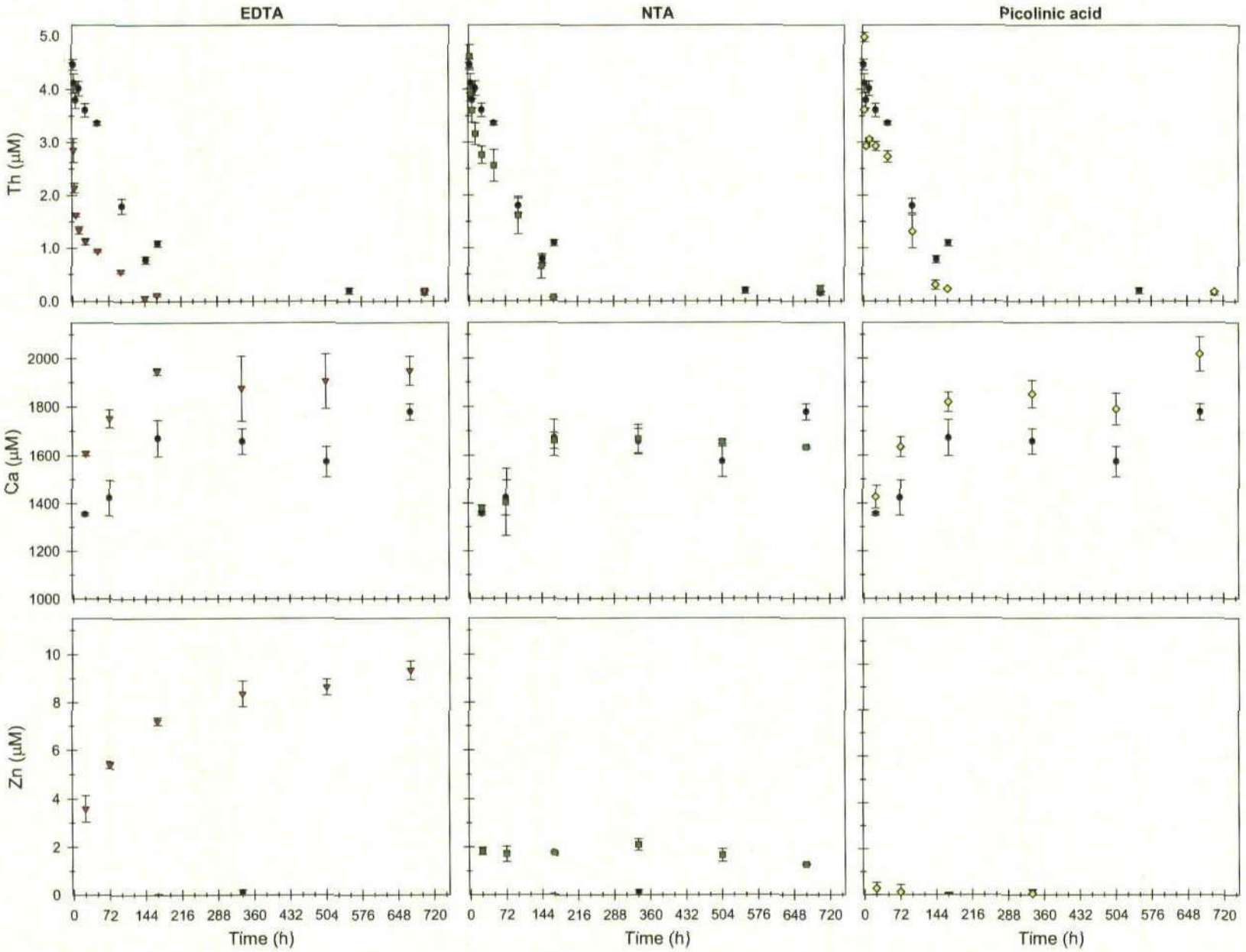

Figure 3. 6 Kinetics of Th (5 µM) sorption to natural sand (top row) and desorption of Ca (middle row) and Zn (bottom row) from the sand surface into MilliQ water (●) and into 200 µM EDTA (▼), 200 µM NTA (■) and 200 µM picolinic acid (●) solutions. The error bars represent ± one standard deviation of three replicate samples.

Qualitative identification of species in solution. ESI-MS was used as a sensitive speciation technique to identify the speciation of the Th and metal complexes in the solution phase. High background noise from DOC in the solutions from the natural sand systems prevented useful ESI-MS data from being obtained. However, it was possible to analyse the solutions from the silica systems. The positive and negative ion mode spectra for the solutions containing 200 µM EDTA (Figure 3.7) confirmed that the Fe desorbed from the silica was complexed by EDTA and was identified as $[FeEDTA]^-$ (*m/z* 344). This was also detected as a sodium adduct in the positive ion mode $[Na_2FeEDTA]^+$ (*m/z* 390).

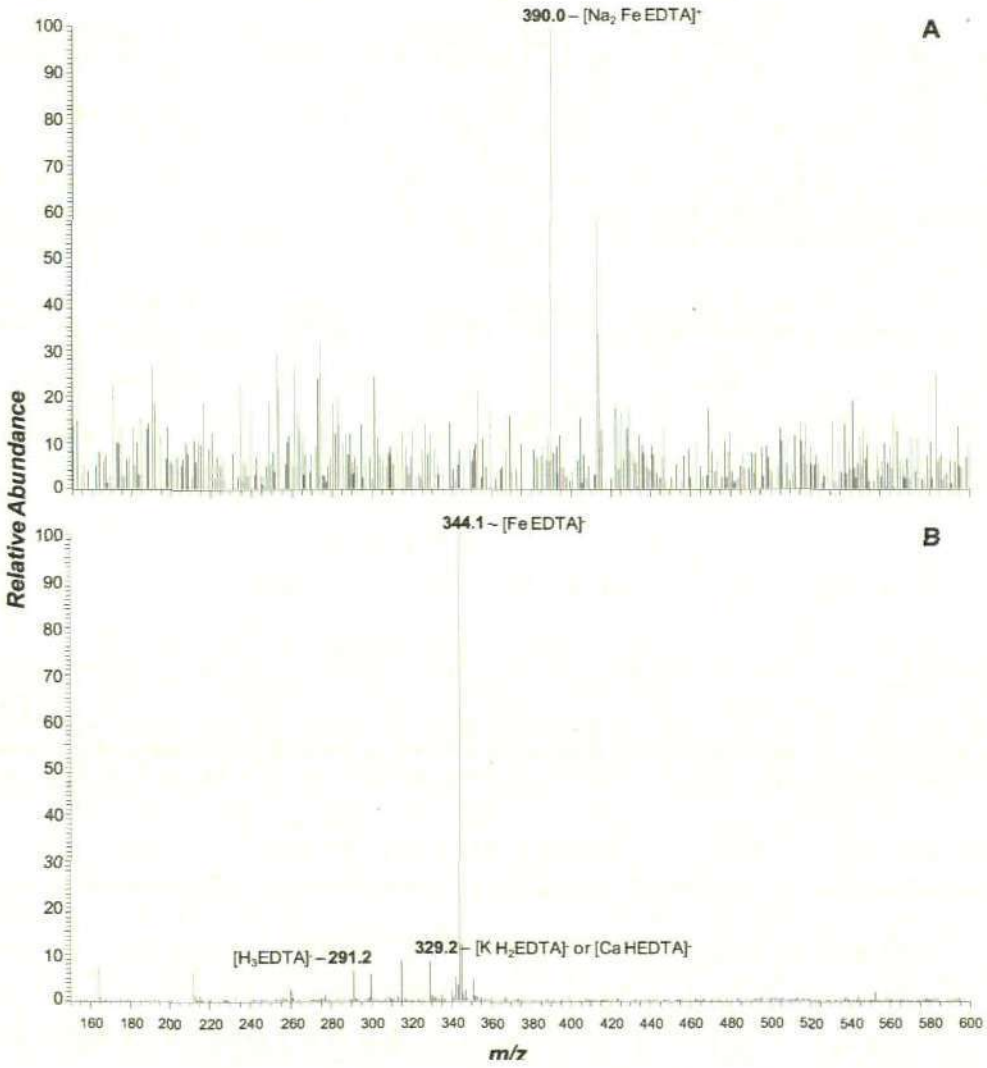

Figure 3. 7 ESI- positive (**A**) and negative (**B**) ion mass spectra for a solution containing 5 µM Th and 200 µM EDTA in contact with silica.

There was also some evidence of Ca- or K-EDTA complexes (*m/z* 329) in the negative ion mode. A small peak assigned as uncomplexed EDTA (*m/z* 291) was also present. Since the Fe-EDTA complex accounted for 20 % of the EDTA in solution, this complex electrosprayed with a much greater efficiency than $[H_3EDTA]^-$. No signals representative of Th species were observed, but the 5 μM Th concentration used was below the detection limit for Th-EDTA and Th-NTA complexes (40 μM; (Cartwright *et al.*, 2007)). However, with 5 μM EDTA in solution, a small peak for $[FeEDTA]^-$ was identified in the negative ion mode, corresponding to a 1.6 μM concentration of Fe desorbed from the silica. These spectra therefore confirmed that EDTA drives Fe desorption directly through complexation.

3.3.4 Modelling

The equilibrium solution phase concentrations of matrix metal cations determined in each sand system (Table 3.4) were included in speciation calculations with 5 μM Th to examine the theoretically predicted competition between the solution phase metals and Th for the ligands at two different concentrations, 200 and 5 μM. The model predicted that 100 % of the Th, Zn, Mn and Fe would be complexed by EDTA, but only 10 % of the Ca (i.e. 180 μM Ca) would be present as an EDTA complex. This suggests that Ca does not compete with Th for EDTA in this system. Lowering the EDTA concentration to 5 μM, to introduce competition between metals and Th for EDTA, resulted in a fairly even level of complexation with 36, 34 and 28 % of the EDTA bound to Th, Zn and Fe respectively. Ca remained uncomplexed in solution.

Table 3. 4 Concentrations of matrix metal cations used for the speciation calculations of each organic complexing agent system.

Cations	Concentration (μM)		
	EDTA	*NTA*	*picolinic acid*
Ca^{2+}	1800	1500	1700
Zn^{2+}	7	1.7	0
Mn^{2+}	3	0.5	0.3
Fe^{3+}	3	1.5	1
K^{+}	250	225	250
Mg^{2+}	350	340	400

With NTA, again 100 % of the Zn and Fe, and 12 % of the Ca were predicted to be complexed, along with 65 % of the Th (3.25 μM) and 53 % of the Mn. Removing Ca from the calculations resulted in full complexation of Th in the model output, demonstrating that Ca does compete to an extent with Th for NTA. Moreover, when the NTA concentration was reduced to 5 μM, NTA complexed Zn, Ca and Fe preferentially over Th (32, 27, 38 and 2 % of the NTA concentration respectively). Picolinic acid is not included in the Visual MINTEQ database and hence no prediction was obtained for the formation of picolinic acid complexes with these matrix metals.

These calculations indicate that Zn and Fe offers greater competition for EDTA or NTA than Ca in these systems. Therefore, metal exchange of the Th complexes at the sand surface is likely to involve Zn. Additionally, given that metal competition for the ligands is insufficient to explain the sorption of Th in these systems, the attraction of Th to the surface binding sites provides the thermodynamic driving force behind metal exchange.

3.3.5 Mechanisms of Th interactions

The experiments demonstrated that Th complexes of EDTA, NTA and even picolinic acid are formed in solution and solubilise Th in the presence of silica. However, the effect of the ligands was highly dependent on the solid phase present and, in the natural sand systems, the ligands had the opposite effect on Th solubility by enhancing the Th sorption rate. Since EDTA has the highest affinity for Th it appears that the higher the Th-ligand complex stability constant, the greater the effect on the Th sorption rate. This is consistent with the results from the 24 h experiments, with faster sorption rates seen with a) higher ligand concentrations and b) pre-equilibration of the Th and ligand solutions. Therefore, the greater the amount of Th-ligand complex formed, the faster Th sorbs to the surface. Matrix metal desorption was also dependent on the ligand used, and EDTA produced a significant excess release of Ca and Zn in the first 24 h; while NTA resulted in increased, but relatively lower, Zn concentrations and picolinic acid increased the Ca concentration. The data therefore suggest that Th-ligand complexes interact with the sand surface more readily than uncomplexed Th, and that metal exchange between Th-EDTA or -NTA and Zn is a faster process than sorption of inorganic Th species.

Comparison of the experimental data and model outputs also demonstrates that the affinity of Th for the solid phases was the thermodynamic driver behind this process, as the concentrations of matrix metals solubilised would not destabilise any Th-EDTA, or the majority of the Th-NTA, complexes. The presence of picolinic acid enhanced Th sorption to a similar extent to NTA but the data showed high levels of picolinic acid sorption and that Ca was the only matrix metal that increased in concentration in solution. Given that

the results from the silica system demonstrated the formation of Th-picolinate complexes to an extent, the data suggest that the formation of this complex enhances sorption.

3.4 Conclusions

The wide range of analytical techniques used in this work has allowed a full characterisation of the interactions between Th, organic complexing agents and solid phases. The experiments with silica demonstrated the capacity of the complexing agents to form complexes with Th in solution in the presence of sorption sites, and to enhance its solubility in environmental systems. However, as the complexity of the systems increased to include a natural solid phase, the complexing agents increased the rate of Th sorption, lowering its predicted environmental mobility in dynamic systems. Determination of complexing agent sorption and desorption of other cations from the solid surface, along with data from increasing the concentration of ligand, pre-equilibrating the Th-ligand solutions, and modelling the systems has provided a detailed understanding of the processes taking place and the driving forces of the reactions. Overall, the study has demonstrated the complexity of the interactions between radionuclides and complexing agents, even in relatively simple environmental systems, where for example other complexing agents, such as DOC, are limited. It has also demonstrated the dependence of the process on the organic complexing agent and its relative affinity for the radionuclides and matrix metals with respect to the affinity of the cations for the solid surface sites.

Chapter 4

Comparison of the effect of organic complexing agents on U, Sr and Cs interactions with natural sand

4.1 Introduction

The sorption of key radionuclides, such as Cs, Sr and U(VI), to natural solid phases has been widely studied (e.g. Dyer *et al.* (2000), Echevarria *et al.* (2001), Zachara *et al.* (2002)). However, the effect of organic complexing agents such as EDTA, NTA and picolinic acid on their sorption behaviour is less well known. Chapter 3 demonstrated that EDTA, NTA and picolinic acid influenced Th sorption (to silica) or sorption kinetics (to natural dune sand), and that the higher the affinity of the ligand for Th, the more marked the effect. Cs, Sr and U(VI) have different stability constants with the ligands of interest, thus the relative effects of the ligands in comparable systems will provide an insight into direct and indirect ligand-induced changes in solubility.

Therefore, the aim of this chapter was to study and compare the effect of 3 organic complexing agents on the sorption of 3 different radionuclides, with different oxidation states, under the same experimental conditions. Cs(I) and Sr(II) as important fission products, and U(VI) as a representative actinide, were selected for the study since they encompassed a wide range of oxidation states. As in Chapter 3, EDTA, NTA and picolinic acid were the complexing agents selected. This will allow a direct comparison of the results with the effects reported for Th(IV), and will include 3 different ligand denticities. Therefore, the effect of the complexing agents on i) radionuclide sorption on artificial silica and natural sand and ii) the kinetics of the sorption on natural sand was quantified for the 3 radionuclides. Visual MINTEQ was used to compare the predicted solution phase speciation with the experimental results.

4.2 Experimental

4.2.1 Radionuclides, organic complexing agents and solid phases

All labware was washed and stored as described in 3.2.1 and solutions and batch experiments were always prepared using MilliQ water (Millipore; 18.2 MΩ cm^{-1}). Stable isotopes of Cs and Sr were used in these experiments and solutions were prepared from the respective chloride salts obtained from Sigma-Aldrich (Gillingham, Dorset, UK). Uranium was obtained as the nitrate salt from BDH Chemicals Ltd (Poole, England) and solutions were prepared following the same procedure as for the Th nitrate salt described in 3.2.2. EDTA sodium salt was obtained from Fisher Scientific (Loughborough, UK) and NTA sodium salt and picolinic acid were obtained from Sigma-Aldrich (Gillingham, Dorset, UK). The natural and synthetic solid phases (silica and natural sand) used in these experiments were the same as those used in Chapter 3, where their characteristics have been described (see 3.2.2 and 3.3.1).

4.2.2 Experimental design

All batch experiments were prepared in the same manner and using the same conditions as those adopted for the Th batch experiments (see section 3.2.3). Nevertheless, Table 4.1 summarises the conditions of the experiments carried out in this chapter under which Cs, Sr and U sorption and the effect of organic complexing agents were studied. Stable Cs and Sr were used in the experiments, thus the molar concentrations used would correspond to high activity concentrations of the radioisotopes (2×10^7 Bq L^{-1}). However, in natural systems, there is always a background level of Cs and Sr which contributes to the behaviour of the element. For example, Sylvester & Clearfield (1998) reported total Cs

and Sr concentrations of 1.5 x 10^{-8} and 1.5 x 10^{-6} M respectively in Hanford groundwater. The 5 μM U concentration used is less than that found in the groundwater of the more contaminated zones of Hanford (~12 x 10^{-6} M U) (Hartman *et al.*, 2009). Therefore the concentrations used were environmentally representative.

Table 4. 1 Experimental conditions for the sorption experiments. Rad = radionuclide; OCA = organic complexing agent.

System	Effect studied	Solid phase (g)	Rad (μM)	OCA (μM)	Incubation time (h)
Silica/Rad	Sorption	5	5	-	168
Sand/Rad	Sorption kinetics	5	5	-	From 0.5 to 168
Silica/OCA	Sorption	5	-	5, 200	168
Silica/Rad/OCA	Effect of OCA concentration on Rad sorption	5	5	5, 200	168
	Effect of OCA on matrix metals desorption	5	5	5, 200	168
Sand/Rad/OCA	Sorption kinetics	5	5	500	From 0.5 to 168
	Effect of OCA concentration on Rad sorption	5	5	5, 20, 80, 200	24
	Effect of solution pre-equilibration (24 h) on Rad sorption	5	5	5, 20, 80, 200	24
	Effect of OCA on matrix metals desorption	5	5	200	168

4.2.3 Analytical methodology

Matrix metal analysis by ICP-OES, organic complexing agent determinations by IC and UV spectrometry, and qualitative complex determination of silica experimental solutions by

ESI-MS were carried out as described in Chapter 3. Radionuclide determination by ICP-MS followed the same procedure as that for the Th determination, but in this case 10,000 μg mL^{-1} Cs and Sr (Aristar) and 1,000 μg mL^{-1} U (Alfa Aesar) plasma emission standard solutions were used to prepare the standard solutions. The LOD (as defined in section 2.3.1) for the 3 radionuclides was always < 0.5 nM.

4.3 Results and Discussion

4.3.1 Silica system

Radionuclide sorption and organic complexing agent effect. The sorption behaviour of 5 μM Cs, Sr and U to silica in the presence of 40-fold excess organic complexing agent was studied after a 168 h incubation time.

Caesium. Figure 4.1 shows that, in the absence of ligands, Cs had a fairly low affinity for the silica surface and 76 ± 2 % remained in solution. The presence of excess ligand did not affect Cs sorption, which is consistent with the very low stability constants of the Cs-EDTA and Cs-NTA complexes (Table 4.2).

Strontium. Sr showed a lower affinity for the silica than Cs, with 91 ± 3 % of the initial Sr concentration remaining in solution. However, 40-fold excess EDTA enhanced Sr solubility further, resulting in 98 ± 1 % of the Sr remaining in solution. Excess NTA had the opposite effect and slightly reduced Sr solubility (80 ± 1 % in solution), while picolinic acid had no effect.

Uranium. U showed the highest affinity of the three elements for the silica (16 ± 1 % in solution) and all of the ligands enhanced U solubility significantly. Excess EDTA and picolinic acid had the greatest effect and kept 65 ± 4 and 57 ± 2 % of the U in solution respectively. NTA solubilised U to a lesser extent (40 ± 6 %), showing a more limited effect than EDTA, which is consistent with the higher stability constant of U-EDTA species (Table 4.2). Picolinic acid had a greater effect than NTA, but there are no reported U-picolinate stability constants.

The results indicate that Sr-EDTA and -NTA, and U-EDTA, -NTA and -picolinic acid complexes form in the silica system and, with the exception of Sr-NTA, enhance the solubility of the radionuclides. None of the interactions were as marked as those with Th (Chapter 3), which is consistent with the known stability constants.

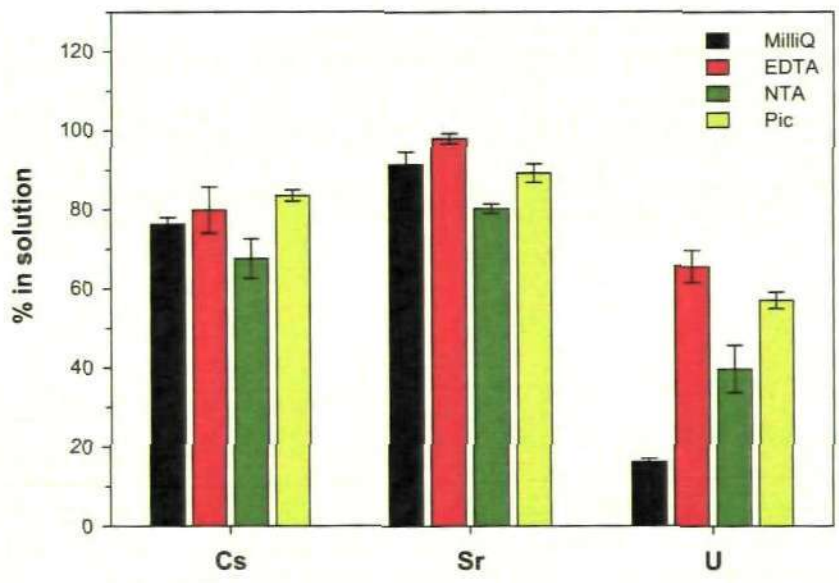

Figure 4. 1 Cs, Sr and U sorption to silica in MilliQ and in 200 μM EDTA, NTA and picolinic acid solutions. The error bars represent one standard deviation of three replicate samples.

Table 4. 2 Stability constants (log *k*) for EDTA, NTA and picolinic acid and Cs, Sr, U and Th. Data obtained from Cartwright *et al.* (2007); Serne *et al.* (2002) and Stumm & Morgan (1996).

Cation	EDTA		NTA		Picolinic acid	
	Species	*Log k*	*Species*	*Log k*	*Species*	*Log k*
Cs^{+}	CsL^{3-}	1.05	CsL^{2-}	0.84		
Sr^{2+}	SrL^{2-}	10.5	SrL^{-}	6.3	SrL^{+}	1.8
	$SrHL^{-}$	14.9			SrL_2	3.0
UO_2^{2+}	UO_2HL^{-}	19.7	UO_2L^{-}	10.8		
	UO_2L^{2-}	13.7				
	$(UO_2)_2L$	15.2				
Th^{4+}	ThL	26.8	ThL^{+}	15.1 / 19.5		
	$ThHL^{+}$	28.8	ThOHL	6.49		
	$ThOHL^{-}$	19.5				

4.3.2 Natural sand

Sorption kinetics and effect of excess complexing agent.

Caesium. Cs rapidly sorbed to the natural sand (Figure 4.2 A) and equilibrium was reached after 24 h, with 96 % Cs sorbed. The presence of excess complexing agent in solution had no effect on the rate of Cs uptake or the equilibrium position, which is consistent with the results from the silica system.

Strontium. The controls with no ligand and no radionuclide demonstrated that natural Sr slowly desorbed from the sand into solution (Figure 4.2 B – "natural Sr") and the presence of the ligands did not change the desorption profile significantly (data not shown, $p \approx 0.50$, 0.09 and 0.87 for 200 µM EDTA, NTA and picolinic acid respectively, paired t-test). Therefore, in the systems to which Sr was added, including the MilliQ "blank", the net Sr concentration was determined and is presented in Figure 4.2 B as a percentage of the Sr

concentration added. All the profiles followed the same trend as the controls, dominated by Sr release rather than uptake, demonstrating that sorption of the Sr added was rapid. From 2 h onwards, there was consistently 26 ± 3, 37 ± 4 and 40 ± 7 % of the Sr added in solution above the natural Sr background for the MilliQ, excess EDTA and picolinic acid experiments, respectively. In contrast, there was no significant difference between the Sr concentration in the NTA system and the natural Sr control, suggesting that NTA strongly enhanced Sr sorption.

Uranium. U showed a rapid initial uptake with about 13 % of the U remaining in solution after 5 h (Figure 4.2 C), followed by slower sorption, and equilibrium was reached after 48 h (< 6 % in solution). As seen for Th (Chapter 3), the addition of excess organic complexing *agents enhanced the rate of sorption to the natural dune sand significantly, despite* enhancing U solubility in the presence of silica. Excess NTA slightly increased the rate of U sorption while EDTA and picolinic acid had a larger effect and the systems reached *sorption equilibrium after 5 h. At equilibrium, as for Th, the ligands did not affect the* solubility of U.

Therefore, Cs and Sr showed rapid sorption to the natural sand and the ligands did not affect the rate of uptake, although they did impact on the equilibrium solubility of Sr. However, U and Th (Chapter 3) showed slower sorption kinetics and the presence of the ligands enhanced their sorption rates, although not their overall solubility at equilibrium. The results from the silica systems identified that excess EDTA and picolinic acid had comparable impacts on the solubility of U, and these ligands had a very similar impact on U sorption kinetics in the natural sand systems.

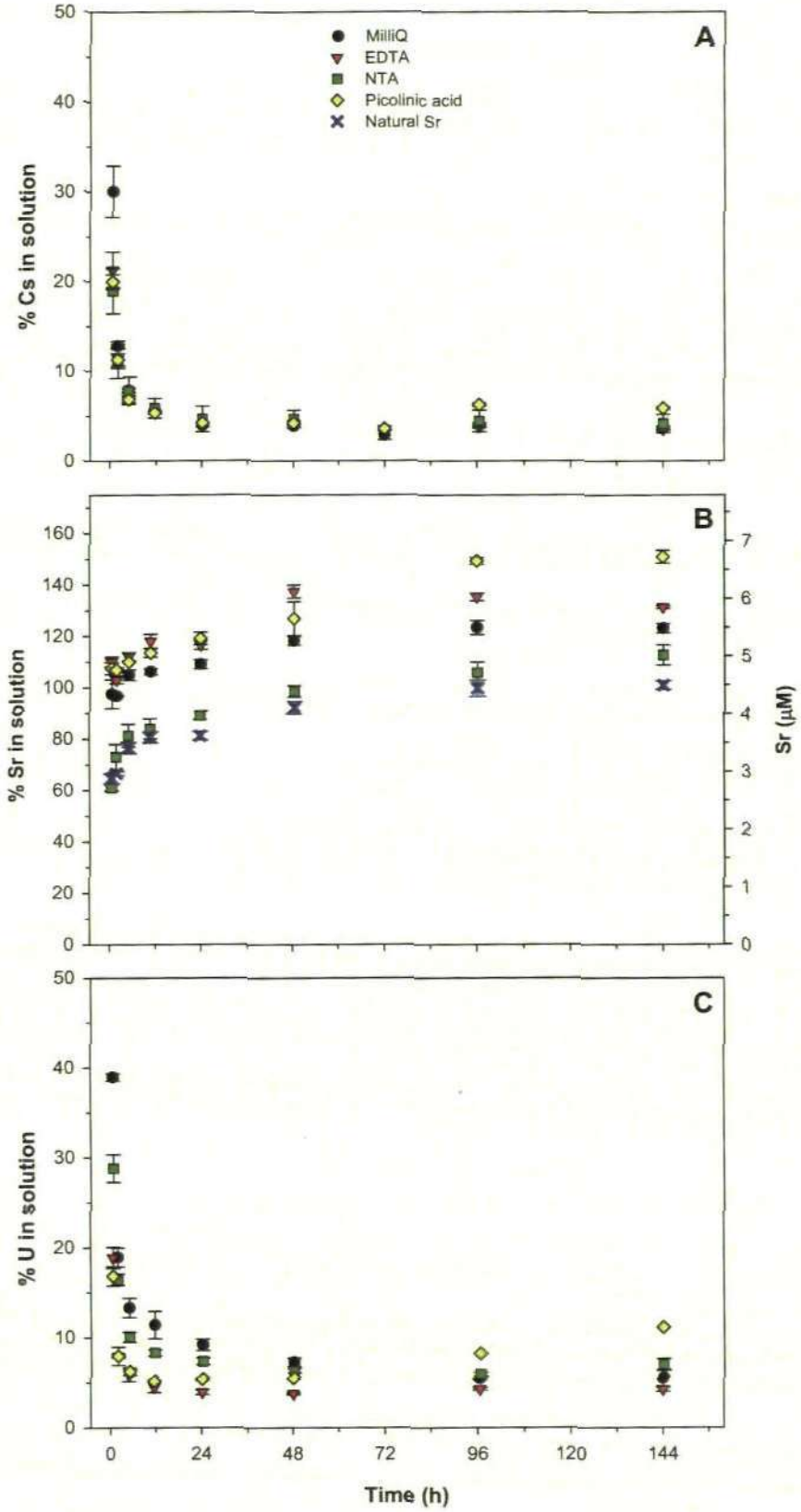

Figure 4. 2 *Effect of organic complexing agents on the sorption kinetics of* **A**) 5 μM Cs, **B**) 5 μM Sr *and* **C**) 5 μM U. The % radionuclide remaining in solution is plotted against time (h) for the experiments containing solutions of MilliQ (●), 500 μM EDTA (▼), 500 μM NTA (■) and 500 μM picolinic acid (◆). **B**) also shows the desorption of natural Sr (×) in μM and as % of the Sr added. The error bars represent ± one standard deviation of three replicate samples.

Effect of complexing agent concentration and solution pre-equilibration. Since Cs and Sr sorption reached equilibrium within 24 h, the effect of complexing agent concentration and pre-equilibration of the radionuclide and complexing agent solution on the Cs and Sr sorption was assessed using a 24 h incubation time.

Caesium. Cs sorption was not affected by the ligand concentration and, as expected, pre-equilibration of the Cs and complexing agent solution did not change the Cs solubility significantly in any of the systems.

Strontium. No significant changes were observed between pre- and not pre-equilibrated experiments for any of the 3 organic complexing agent solutions with Sr, thus the averages of the two results for 1- to 40-fold excess ligand were used in Figure 4.3. The 100-fold excess data obtained for 24 h (Figure 4.2) was also included. Equimolar and a 4-fold excess of complexing agents had no effect on Sr solubility. However, with higher ligand concentrations (80 and 200 μM), enhanced solubilisation (with EDTA) and sorption (with NTA) of Sr were seen, which followed the previous observations with EDTA and NTA in the silica system. Increasing the NTA concentration from 200 to 500 μM resulted in further sorption of Sr, however, the equivalent increase in EDTA concentration did not increase Sr solubility further. Picolinic acid concentrations ≤ 200 μM had no significant effect on Sr sorption after 24 h, but a clear effect was seen with 500 μM picolinic acid. This suggests that a very large excess of picolinic acid (100-fold) is required to significantly affect Sr solubility. This is generally consistent with the findings of Serne *et al.* (2002), that picolinate concentrations had to be > 10^{-3} M to significantly lower the sorption of radionuclides (10^{-5} M) to an iron oxide coated sand.

Overall, the increased effect seen with increasing concentration, and the lack of a pre-equilibration effect, again suggests rapid complex formation and that the ligands had a net effect on the Sr solubility, rather than the sorption rate.

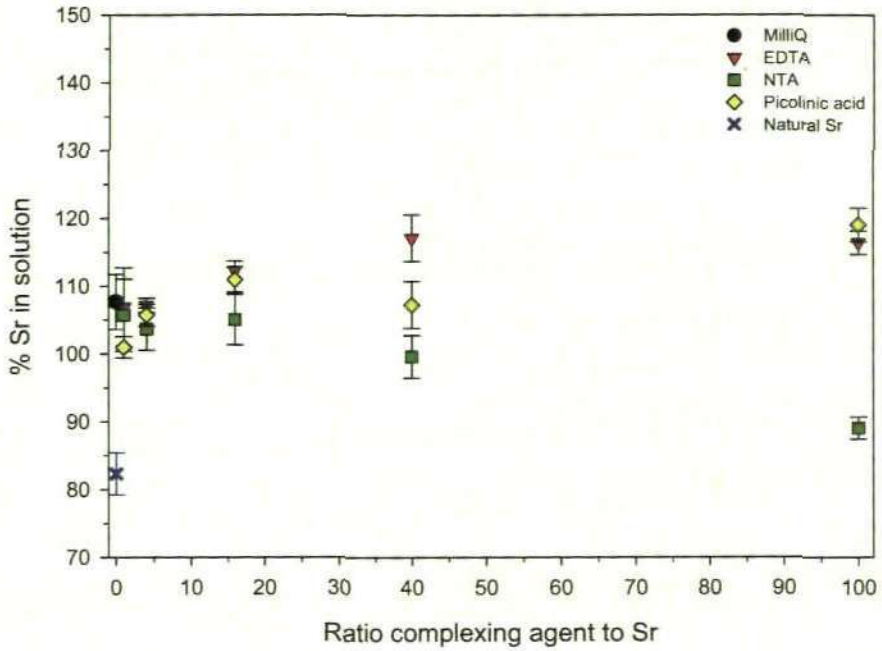

Figure 4. 3 Effect of organic complexing agent concentration on Sr (5 μM) sorption after 24 h incubation time. The average % of Sr in solution for pre- and not pre-equilibrated experiments is plotted against the ratio of complexing agent to Sr for experiments with solutions containing MilliQ (●), EDTA (▼), NTA (■) and picolinic acid (◆). The natural Sr (×) is represented as % of Sr concentration used. The error bars represent ± one standard deviation of three replicate samples.

Uranium. U showed slower sorption kinetics than Cs and Sr and reached equilibrium after 48 h, thus the 24 h incubation time provided insight into the effect of ligand concentration and solution pre-equilibration on the U sorption rate. Figure 4.4 A shows that equimolar EDTA slightly enhanced the rate of U sorption and 9 ± 2 % of U remained in solution after 24 h; however, higher EDTA concentrations increased its sorption rate further and equilibrium was reached in these systems (3.9 ± 0.3 % U in solution). Pre-equilibration of the equimolar U-EDTA solution (24 h) resulted in the system reaching

the U sorption equilibrium. Since equilibrium was reached with the higher EDTA concentrations, pre-equilibration did not have any further effect.

Uranium sorption was affected by NTA and picolinic acid to a similar extent and showed a different pattern to that of U and EDTA (Figure 4.4 B and C). Uranium was more soluble with equimolar and 4-fold excess ligand concentrations after the 24 h period, suggesting the ligands slowed U sorption. Higher concentrations of the ligands enhanced the rate of U sorption, but sorption equilibrium was not reached in any of these systems (7 % U in solution). However, the pre-equilibration of the U-NTA and U-picolinic acid solutions enhanced U sorption further for all concentrations and the 16- and 40-fold excess systems reached sorption equilibrium within the 24 h period. The reason why low concentrations enhanced U solubility is not clear. As with Sr, picolinic acid appears to be most effective at high concentrations, thus it has a similar effect on U solubility as NTA at low concentrations (≤ 80 μM) (Figure 4.4 B) and approaches the effect of EDTA at high concentrations (≥ 200 μM) (Figure 4.2 C).

Despite the increase in U solubility at low ligand concentrations, the enhanced U sorption with increasing concentration and solution pre-equilibration suggest that the formation of the complexes affects the rate of U sorption, as was seen with Th in the natural sand system (Chapter 3).

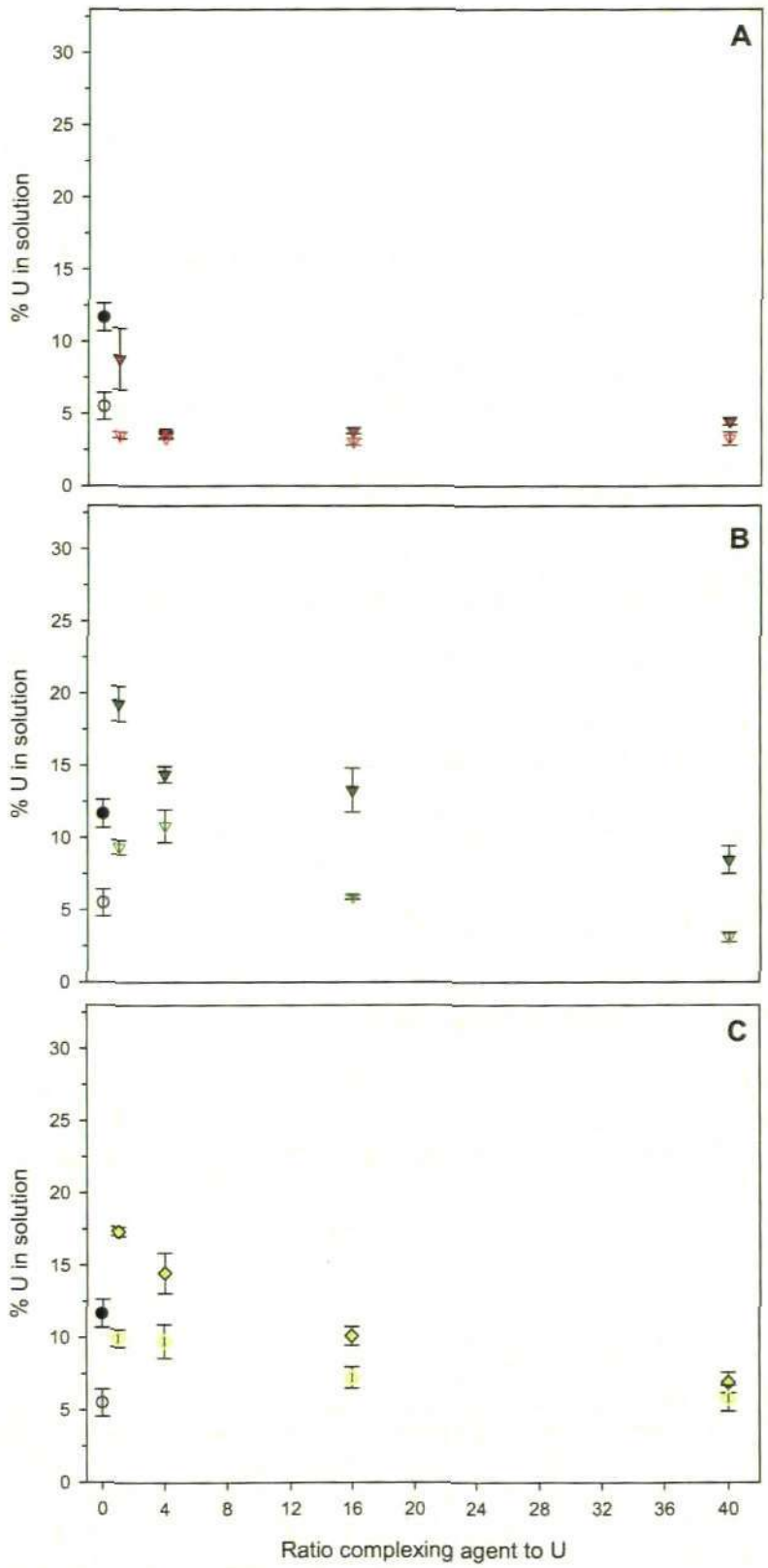

Figure 4. 4 Effect of organic complexing agent concentration and solution pre-equilibration on U (5 μM) sorption after 24 h incubation time. The % U remaining in solution is plotted against the molar ratio of complexing agent to U for experiments with solutions containing MilliQ at 24 h (●) and at sorption equilibrium (○, 552 h), and for not pre-equilibrated (filled symbols - ▼, ■, ◆) and pre-equilibrated (open symbols - ▽, □, ◇) experiments containing solutions of **A**) EDTA, **B**) NTA and **C**) picolinic acid at 24 h. The error bars represent ± one standard deviation of three replicate samples.

4.3.3 Changes in the solution phase

The concentration of excess ligand exceeded the concentration of radionuclides by up to 2 orders of magnitude; therefore, the sorption behaviour of the ligands, as well as their effect on the desorption of matrix metals, were largely independent of the radionuclide present in solution. Consequently, consistent results were obtained from the different radionuclide systems with each complexing agent and solid phase. A maximum of 25 % EDTA and negligible NTA sorbed to either solid phase after 168 h. However, picolinic acid sorbed to a different extent depending on the solid phase, and 25 % was sorbed to the silica surface, while complete removal from solution was observed in the sand systems after the 168 h incubation time.

The metal concentrations desorbed from both the silica and natural sand are equivalent to those reported in Chapter 3 (Tables 3.3 and 3.4).

4.3.4 Modelling

The equilibrium concentration of matrix metal cations determined in the Th sand systems (Table 3.4) along with a 200 µM ligand concentration were included in speciation calculations with 5 µM Cs, Sr or UO_2^{2+} to compare the theoretical extent of complexation of the different radionuclides by the ligands. Picolinic acid is not included in the database and therefore no predictions can be made with this ligand. The model predicted that Cs^+ would remain uncomplexed in the presence of EDTA and NTA.

In the absence of the matrix cations, EDTA is predicted to complex 100 % of the Sr, while only 24 % of the Sr is predicted to be present as an NTA complex. The addition of the cations to the calculations lowered the predicted Sr-EDTA and Sr-NTA complex

percentages to 0.12 and 0.43 % respectively, as the metals (Ca, Zn, Mn and Fe) strongly compete for the ligands.

Again, in the absence of the matrix cations, the model predicted that EDTA would complex 99 % of the UO_2^{2+} in solution, while 92 % would be present as a U-NTA complex. In the presence of the matrix cations, 0.12 and 4 % of the U is predicted to be complexed by EDTA and NTA respectively. It is interesting to note that despite the higher affinity of EDTA for U, the generally high affinity of EDTA for matrix metals ultimately results in the prediction that it binds less U than NTA.

4.3.5 Comparison and summary of the effect of complexing agents

The speciation model provides an insight into the solution phase competition and can be used alongside the experimental data to consider the key processes determining radionuclide behaviour.

Caesium. The lack of interaction between Cs and the ligands observed experimentally is consistent with the results from the model. However, the experimental data provide evidence that Cs sorption is also not affected indirectly as the ligands solubilise matrix metals and enhance the number of surface binding sites available, despite the reasonable affinity of Cs for the sand.

Strontium. The model predicted that Sr would be complexed by EDTA to a greater extent than NTA in these systems. This is difficult to compare with the experimental data as NTA reduced, and EDTA increased, the solubility of Sr in both the silica and sand systems. However, given the model prediction that the ligands would not complex Sr significantly

in the presence of the matrix metals in solution, it appears that Sr interacts with these ligands to a greater degree than predicted. Although there are no stability constants for Sr with picolinic acid, it was clear that picolinate did not affect Sr solubility until it was present in vast excess. Here, when picolinic acid was in 100-fold excess of Sr, it affected Sr to a similar degree as 100-fold excess EDTA.

Uranium. U was predicted to be complexed by EDTA and NTA in the absence of the matrix metals and U solubility increased significantly in the silica systems, which is consistent with this. In the sand system, a similar effect was seen with the ligands as seen previously with Th. The U sorption rate increased in the presence of the ligands, especially EDTA, presumably because EDTA-metal exchange is more rapid than sorption of uranyl ion. The modelling suggests that, in this case, the affinity of EDTA and NTA for the matrix metals would have been sufficient to drive the process. The lesser effect of NTA reflects its lower affinity for U. Although it is not possible to model picolinic acid, the experimental data showed a clear effect on U solubility (silica system) and sorption rate (sand system), suggesting that there is a significant interaction between picolinic acid and U, which was more marked as the picolinic acid concentration increased. These are important experimental data, particularly given the lack of published stability constants for picolinic acid complexes.

The effects of the 3 ligands with the 4 radionuclides studied throughout this thesis are summarised in Table 4.3. The stability of the complexes generally increases with *increasing ionic charge; however, since the penta- and hexavalent actinides are bonded* with two oxygen atoms, giving MO_2^+ and MO_2^{2+}, the actinide complex stabilities decrease in the order IV ≥ VI > III ≥ V (Choppin *et al.*, 2002). In this work, the relative level of

interaction (either increasing or decreasing sorption) varied in the order: $Th^{4+} > UO_2^{2+} > Sr^{2+} > Cs^{+}$, which agrees with the general trend. Another general rule is that the greater the denticity and the charge of a ligand, the higher the stability constant of the metal-ligand complex (Means & Alexander, 1981). EDTA clearly affected the solubility of the radionuclides to the greatest extent and it has the highest denticity of the three ligands. However, the relative effects of NTA and picolinic acid varied from system to system. With silica, the relative effect followed the general trend and EDTA > NTA > picolinic acid, while with natural sand, high concentrations of picolinic acid resulted in a similar effect to EDTA (for Sr and U) and to NTA (for Th), highlighting the potential importance of picolinic acid in contaminated environments.

Table 4. 3 Summary of 200 – 500 μM EDTA, NTA and picolinic acid effect on Cs, Sr, U and Th sorption to silica and sand surfaces. Symbols key: up arrow = increased solubility, down arrow = enhanced sorption and cross = no effect; full arrow = effect at sorption equilibrium, dashed arrow = effect on sorption rate. The differences caused by the ligand are represented in terms of the % of the radionuclide added as follows: one arrow < 10 %, two arrows = 10 – 40 % and three arrows > 40 %.

Radionuclide	Solid phase	Organic complexing agent		
		Picolinic acid	*NTA*	*EDTA*
Cs(I)	Silica	×	×	×
	Sand	×	×	×
Sr(II)	Silica	×	↓	↑
	Sand	↑	↓↓	↑
U(VI)	Silica	↑↑	↑↑	↑↑↑
	Sand	⇣⇣	⇣	⇣⇣
Th(IV)	Silica	↑	↑↑↑	↑↑↑
	Sand	⇣⇣	⇣⇣	⇣⇣⇣

4.4 Conclusions

These experiments have provided a direct comparison of the sorption behaviour of Th(IV), UO_2^{2+}, Sr^{2+} and Cs^+, and an assessment of the relative effects of EDTA, NTA and picolinic acid on the radionuclides. Firstly, it was seen that the strength of the ligand interactions with the radionuclides followed the order Th(IV) > UO_2^{2+} > Sr^{2+}> Cs^+, as predicted from stability constant data.

Cs^+ was not affected directly or indirectly by the ligands in these systems. However, Sr^{2+} showed greater interaction with EDTA and NTA in the presence of the desorbed matrix metals than predicted by Visual MINTEQ. Strontium complexes formed rapidly with EDTA and NTA, and these showed contrasting behaviour, with $SrNTA^-$ showing enhanced sorption and $SrEDTA^{2-}$ showing greater solubility than Sr^{2+}. The kinetics of UO_2^{2+}-ligand binding is slower than for Sr^{2+}, and although the ligands enhanced UO_2^{2+} solubility in the presence of silica, they enhanced the sorption rate in sand. This was consistent with the Th data (Chapter 3), but was less marked, again in line with the relative stability constants of the complexes. Therefore, UO_2^{2+} sorption is slower than metal exchange of UO_2^{2+}-ligand complexes. Elevated concentrations of picolinic acid were found to enhance the solubility of Sr^{2+} and the sorption rate of UO_2^{2+}, demonstrating the potential importance of this ligand.

Overall, the results have shown that organic complexing agents affect radionuclide mobility in a number of ways, and this is dependent on the radionuclide, ligand, and solid and solution phase characteristics. The results have demonstrated that the kinetics of sorption, as well as the kinetics of radionuclide-ligand complexation, are important within

complex systems and influence radionuclide mobility. Therefore, even in systems where the ligands have no affect on the thermodynamic equilibrium, the presence of radionuclide-organic complexes could affect the migration of the radionuclide through contaminated land.

Chapter 5

Evaluation of electrospray ionisation-mass spectrometry as a technique for the quantitative study of competitive interactions in a ternary Th-Mn-EDTA system

5.1 Introduction

The extent to which ligands complex radionuclides in a given system is a function of the relative concentrations of the radionuclide, the ligand and other metal/radionuclides in the system, and the stability constants of the various radionuclide/metal-ligand complexes. Erk *et al.* (1996) demonstrated the importance of metal ion competition in natural waters, with competition for EDTA resulting in a decrease in the Mn-EDTA complex formed. Exchange reactions can involve surface-adsorbed metals, for example Fe(II) and Zn(II) have been shown to displace Co(II) and Pb(II) and Cu(II) from EDTA complexes in subsurface (Zachara *et al.*, 2000) and marine (Davis *et al.*, 2000) sediments respectively. Despite the importance of EDTA in industrial waste streams, including low and high level nuclear waste, there have been no qualitative or quantitative speciation studies on competitive interactions between metals and radionuclides for EDTA.

Electrospray ionisation – mass spectrometry (ESI-MS) has been used in the study of equilibrated Cu, Pb, Cd, Al and Fe(III)-EDTA complexes (Baron & Hering, 1998) and, more recently, in the study of radionuclide speciation in the presence of anthropogenic organic complexing agents such as EDTA and NTA (Cartwright *et al.*, 2007; May, 2009) and siderophores (Keith-Roach *et al.*, 2005). Despite the fact that the quantification of speciation information obtained by ESI-MS remains a significant challenge (Di Marco & Bombi, 2006; Stewart, 1999), simple inorganic ions (Agnes & Horlick, 1994b; Barnett & Horlick, 1997) and the complexation of Ni by EDTA as a function of the free Ni^{2+} in solution (Olesik *et al.*, 1997) have been successfully quantified using an appropriate internal standard. Ni(II) as an EDTA complex has also been used as an internal standard

for the quantification of Sr-EDTA complexation reactions (Wang & Agnes, 1999). A quantitative assessment of the complexation of Eu by small organic ligands has also been achieved by Plancque *et al.* (2005). Nevertheless, these studies assumed that the measurements of the ion current in the gas phase quantitatively represented the solution equilibrium and that there were equal signal responses for different charged complexes containing the same ligand when measuring the relative amounts of complexed ligand. These assumptions were applied by Baron & Hering (1998) who used calibrations from single component aqueous solutions to successfully quantify uncomplexed EDTA and *metal–EDTA complexes by ESI-MS.*

Therefore, the aim of this chapter was to assess whether the assumptions made in applying quantitative ESI-MS to metal-ligand complexes are valid for the Th-Mn-EDTA ternary system, and thus the extent to which ESI-MS can be used as a quantitative tool in speciation studies to elucidate competitive interactions. EDTA was selected as a common co-contaminant and strong complexing agent and Th(IV) as model actinide. The competition between Th and Fe(III) for EDTA has been investigated using ESI-MS by May (2009), therefore Mn(II) was selected for this study as another common soil matrix metal. The objectives were to compare one component (EDTA), two component (Th-EDTA and Mn-EDTA) and three component (Th, Mn and EDTA) systems in terms of the species present, quantification and how the instrumental response for species varied according to solution composition, and to compare the quantitative data for Th and Mn complexation by EDTA in competitive systems with data predicted by theoretical speciation models.

5.2 Experimental

5.2.1 Reagents and sample preparation

All plasticware used was soaked in 2 % v/v Decon overnight, rinsed with MilliQ water (Millipore, 18.2 MΩ cm^{-1}), soaked in 10 % m/v hydrochloric acid (HCl) overnight and then rinsed thoroughly again with MilliQ water. Plasticware was then left to dry in a laminar flow hood and stored in double zip lock plastic bags to avoid contamination.

Sample and standard preparation was carried out in an ISO 9001:2000 acredidated laboratory, and solutions were always carried out under laminar flow (Class 100) to minimise contamination. EDTA sodium salt was obtained from Fisher Scientific (Loughborough, UK). Thorium nitrate and manganese chloride AnalaR grade salts were obtained from BDH Chemicals Ltd (Poole, England).

Fresh stock solutions of 5 – 10 mM metal, radionuclide and complexing agent were prepared in MilliQ water, and then diluted and mixed in different molar concentrations to obtain the experimental ratios used. During the optimisation and species characterisation steps, solutions were left overnight to equilibrate prior to analysis. When studying the complexation rate, sub-samples were initially transferred to the instrument with a short post-mixing delay of 1 – 2 min, and then sub-samples were measured over 24 h. Solutions for other experiments were left to equilibrate overnight (always > 12 h). To keep the systems as simple as possible, the pH was not adjusted and, instead, was measured in each solution using a conventional pH meter (Mettler Delta 340). Stocks and sample solutions were not acidified in any of the experiments; therefore potential precipitation of Mn and Th in the presence of EDTA was investigated using ICP-MS. The concentrations

of both metals in solution did not change significantly over a 48 h period after mixing, thus precipitation was not an issue in these systems.

5.2.2 Instrumentation

Analyses were carried out using manual flow injection of samples (5 µL sample loop metal-free Rheodyne injector, model number 9125, CA, USA) into the mobile phase delivered at 150 µL min^{-1} using a P580A binary pump (Dionex Softron GmbH, Germering, Germany). Flow injection was selected as an effective and clean method of introducing the sample to the instrument, thus reducing the risk of cross contamination. Chromasoln Plus HPLC water was used as the mobile phase and Chromasolv Plus HPLC methanol (Sigma-Aldrich) was used to clean the system before and after each day of analysis. These flow injection parameters resulted in the greatest sensitivity and cleanest spectra and were determined in preliminary experiments in which the flow rate (50 – 175 µL min^{-1}) and composition of the mobile phase (0 – 100 % v/v methanol/water) were varied. Mass spectrometry analysis was performed using an ion trap mass spectrometer fitted with an electrospray interface (ThermoQuest Finnigan Mat LCQ, San Jose, CA, USA) and Xcalibur 1.0 software. Mass spectra were generally obtained over a mass to charge (*m/z*) range from 50 to 2000. All analyses were performed in triplicate (three injections per sample) and peaks were integrated over 20 s to provide comparable data using QualBrowser software. Data were then processed for relevant *m/z*.

5.3 Results and discussion

5.3.1 EDTA, Mn-EDTA and Th-EDTA systems

Species identification. Aqueous solutions containing 1 mM EDTA, 1 mM EDTA with 0.4 mM Th and 1 mM EDTA with 0.8 mM Mn were initially analysed in both the positive and negative ion modes to identify the species present. The pH of these solutions was within the range 3.0 and 3.5. Table 5.1 summarises the main spectral peaks observed in the two modes and the possible corresponding species in solution. The positive ion mode method gave the most information-rich spectra and most intense signals for all EDTA, Th- and Mn-EDTA solutions, thus it was selected as the main working mode for this study.

The formation of adducts in the ionisation source involving matrix ions (e.g. Na^+ or NO_3^-), as found here, is well documented (Di Marco *et al.*, 2003; May, 2009; Schug & McNair, 2003). Polymerisation also can occur during the electrospray process (Di Marco & Bombi, 2006), and dimerisation of both EDTA and Mn-EDTA species was identified. Optimisation of instrument parameters can reduce the formation of dimers (see section *Optimisation of instrumental parameters*). In the Th-EDTA solution, the species were consistent with those found by Cartwright *et al.* (2007). The most intense signal in positive ion mode came from $[ThEDTA(OH)]^-$, which was confirmed by a weak signal in the negative ion mode. The bis-EDTA Th complex, $[ThEDTA_2]^{4-}$, gave the second most intense signal, and its relative abundance increased with increasing EDTA concentration. Since each species formed various adducts with H^+ and Na^+, the peak intensities were summed for all quantification experiments.

Table 5. 1 Main complexes/adducts observed in positive and negative ion mode ESI-MS of solutions containing EDTA and EDTA with Th or Mn, and their corresponding solution phase species. The most intense signals are highlighted in bold.

Solution	Main complex/adduct observed (*m/z*)		Corresponding solution phase species
	+ve ion mode	*-ve ion mode*	
EDTA	**$[NaH_4EDTA]^+$ (315)**	$[H_3EDTA]^-$ (291)	$[EDTA]^{4-}$ / $[HEDTA]^{3-}$ / $[H_2EDTA]^{2-}$ / $[H_3EDTA]^-$ / $[H_4EDTA]$
	$[Na_2H_3EDTA]^+$ (337)	$[AlHEDTA]^-$ (315)	
	$[Na_3H_2EDTA]^+$ (359)		
	$[Na_4HEDTA]^+$ (381)		
	$[Na_5H_4EDTA_2]^+$ (695)		$[H_8EDTA_2]$
	$[Na_6H_3EDTA_2]^+$ (717)		
	$[Na_6HEDTA_2(H_2O)]^+$ (733)		
	$[Na_7H_2EDTA_2]^+$ (739)		
	$[Na_7EDTA_2(H_2O)]^+$ (755)		
	$[Na_8EDTA_2(OH)]^+$ (777)		
	$[Na_9EDTA_2]^+$ (783)		
EDTA + Mn(II)	$[MnH_3EDTA]^+$ (346)	$[MnHEDTA]^-$ (343)	$[MnEDTA]^{2-}$ / $[MnHEDTA]^-$
	$[NaMnH_2EDTA]^+$ (368)	$[NaMnEDTA]^-$ (366)	
	$[Na_2MnHEDTA]^+$ (390)		
	$[Na_3MnEDTA(H_2O)]^+$ (429.9)		
	$[Mn_2H_5EDTA_2]^+$ (691)	$[Mn_2H_3EDTA_2]^-$ (689)	$[Mn_2EDTA_2]^{4-}$ / $[Mn_2HEDTA_2]^{3-}$ / $[Mn_2H_2EDTA_2]^{2-}$
	$[NaMn_2H_4EDTA_2]^+$ (713)	$[NaMn_2H_2EDTA_2]^-$ (711)	
	$[Na_2Mn_2H_3EDTA_2]^+$ (735)	$[Na_2Mn_2HEDTA_2]^-$ (733)	
	$[Na_3Mn_2H_2EDTA_2]^+$ (757)	$[Na_3Mn_2EDTA_2]^-$ (755)	
	$[Na_4Mn_2HEDTA]^+$ (779)		
	$[Na_5Mn_2EDTA_2]^+$ (801)		
EDTA + Th(IV)	$[ThH_2EDTA(OH)]^+$ (539)	$[ThEDTA(OH)]^-$ (537)	$[ThEDTA(OH)]^-$
	$[NaThHEDTA(OH)]^+$ (561)	(552)	
	(639)		
	(917)		
	(630.6)		$[ThEDTA]$ / $[ThHEDTA]^+$
	$[Na_2ThHEDTA(NO_3)_2]^+$ (690.6)		
	$[Na_3ThH_2EDTA_2]^+$ (879)	$[NaThH_2EDTA_2]^-$ (833)	$[ThEDTA_2]^{4-}$ / $[ThH_2EDTA_2]^{2-}$
	$[Na_4ThHEDTA_2]^+$ (901)	$[Na_2ThHEDTA_2]^-$ (855)	
	$[Na_5ThEDTA_2]^+$ (923)	$[Na_3ThEDTA_2]^-$ (877)	

Optimisation of instrumental parameters. The instrument settings, such as spray voltage, capillary temperature, capillary (cone) voltage and tube lens offset affect the electrospray efficiency of the species as well as the formation of adducts and dimers during the electrospray process (Cech & Enke, 2001; Di Marco & Bombi, 2006). EDTA and Mn-EDTA dimeric species were identified in the positive ion mode (Table 5.1) and they are likely to be an artefact of the electrospray process. Therefore, in order to reduce the dimer spectral abundance of the Mn-EDTA complex, the instrumental parameters were adjusted in positive ion mode using a pre-equilibrated solution containing equimolar Mn and EDTA (0.5 mM).

An automatic optimisation was first carried out with direct sample infusion into the electrospray chamber. Instrument conditions were automatically changed until the highest intensity for the selected *m/z* (346 for $[MnH_3EDTA]^+$) was obtained. However, as flow injection was used for sample introduction in the experiments, the capillary voltage and tubes lens offset were also manually re-adjusted. These two parameters were selected because of their important effect on species detection. Rellan-Alvarez *et al.* (2008) found that higher signal intensities were detected for a metal-nicotianamine complex at higher voltages, while Planque *et al.* (2005) observed that a higher cone voltage led to fragmentation of the Eu complexes with small organic ligands (glyconic acid, acetic acid). In this work, increasing the capillary voltage from 38 to 63 V and reducing the tubes lens offset from 21 to 11 V improved the monomeric to dimeric Mn-EDTA species signal ratio (Figure 5.1). The instrumental optimisation also improved the electrospray efficiency of the Mn-EDTA monomer species by 30 %. However, the total Mn-EDTA species signal response was 3 times lower than the free EDTA or Th-EDTA signals for a

similar concentration. Differences in electrospray efficiency have been reported previously for different metal complexes of a particular ligand (Baron & Hering, 1998), and although these differences are affected by the instrumental parameters used, they mainly arise from the characteristics of the analyte (Cech & Enke, 2001). Hence, as the best signal response for Mn-EDTA species was obtained with the instrumental parameters given in Table 5.2, they were considered optimal for the positive ion mode and thus used throughout this study.

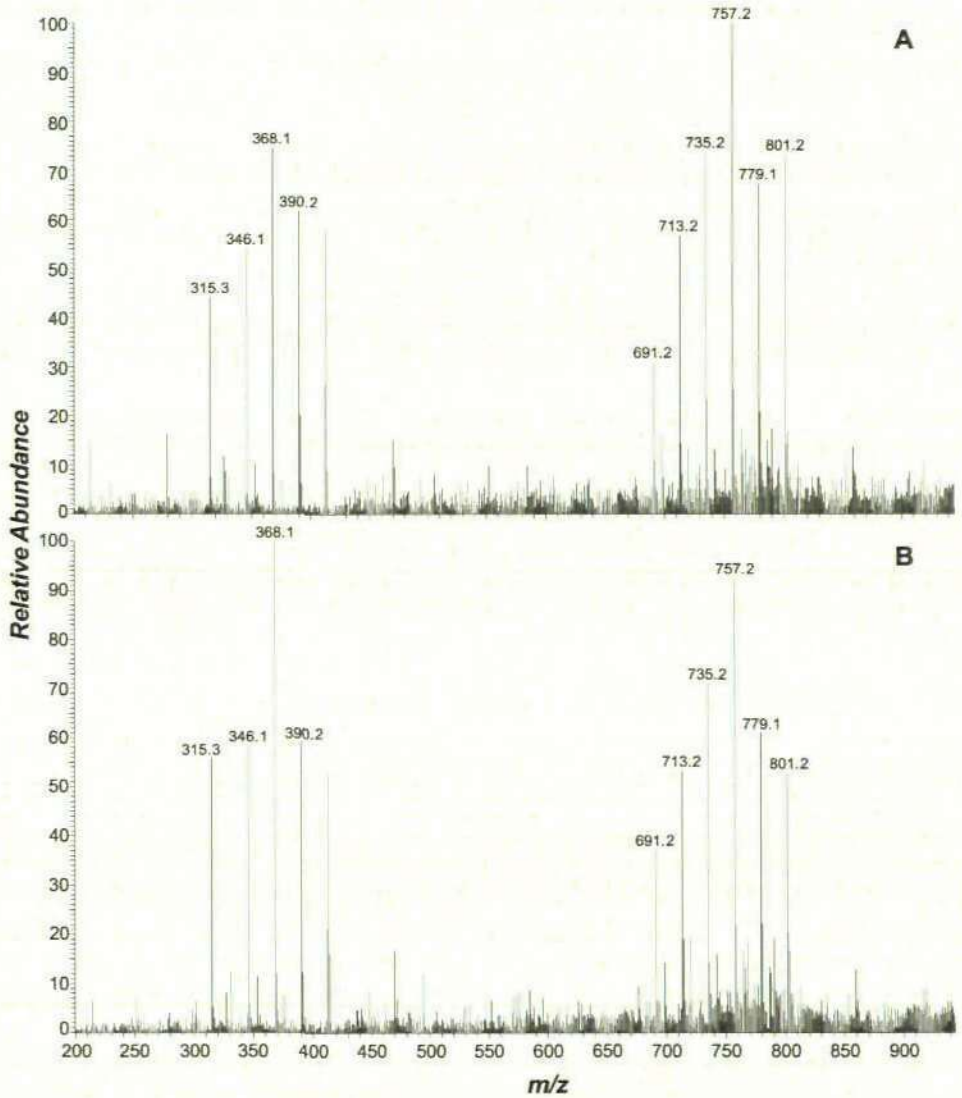

Figure 5. 1 ESI-positive ion mass spectra of a 0.5 mM Mn and EDTA solution with capillary voltage and tube lens offset of **A**) 38 V and 21 V; and **B**) 63 V and 11 V respectively. The highest intensity was for **A**) 1.14 x 10^6 cps and **B**) 1.28 x 10^6 cps.

Table 5. 2 Optimal ESI-MS instrumental parameters in positive ion mode.

Instrumental parameter	Positive ion mode
Capillary (cone) voltage	63 V
Spray voltage	4.57 kV
Tube lens offset	11 V
Capillary temperature	220 °C
N_2 sheath gas flow rate	60 (arbitrary units)
Auxiliary gas flow rate	20 (arbitrary units)

Linear range and calibration. In order to determine the linear range of ESI-MS for the EDTA species, an eight point calibration series (0 – 6 mM) of 3 pre-equilibrated solutions (> 20 h) containing only EDTA, 1:2.5 Th:EDTA and 1:1.25 Mn:EDTA was analysed in the positive ion mode. The calibration graphs (Figure 5.2) show the total sum of counts corresponding to EDTA, Th-EDTA or Mn-EDTA species (summarised in Table 5.1) as a function of EDTA, Th or Mn concentration respectively. These data are based on the inherent assumption that Th and Mn were completely complexed by the excess EDTA used, which is consistent with model predictions and the high stability constants of the complexes (log $k_{[ThEDTA]}$ = 26.7 and log $k_{[MnEDTA]}$ = 15.6). The signals from EDTA, Th-EDTA and Mn-EDTA were saturated at concentrations ≥ 2, 0.75 and 1.6 mM respectively. The lowest concentrations detected were 0.04 and 0.08 mM for Th and Mn respectively with 0.1 mM EDTA. The Th-EDTA linear range was slightly lower than that reported by Cartwright *et al.* (2007) who also assumed that in equimolar Th and EDTA solutions Th was complexed completely over the concentration range studied (0.04 – 2 mM). The linearity of the response was similar for all species with R^2 values of 0.97 for EDTA and

0.98 for Th and Mn-EDTA species. Nonetheless, subsequent calibration series within this linear range always gave R^2 values > 0.98 for the three species. Therefore, all further experiments were carried out within the relevant linear range.

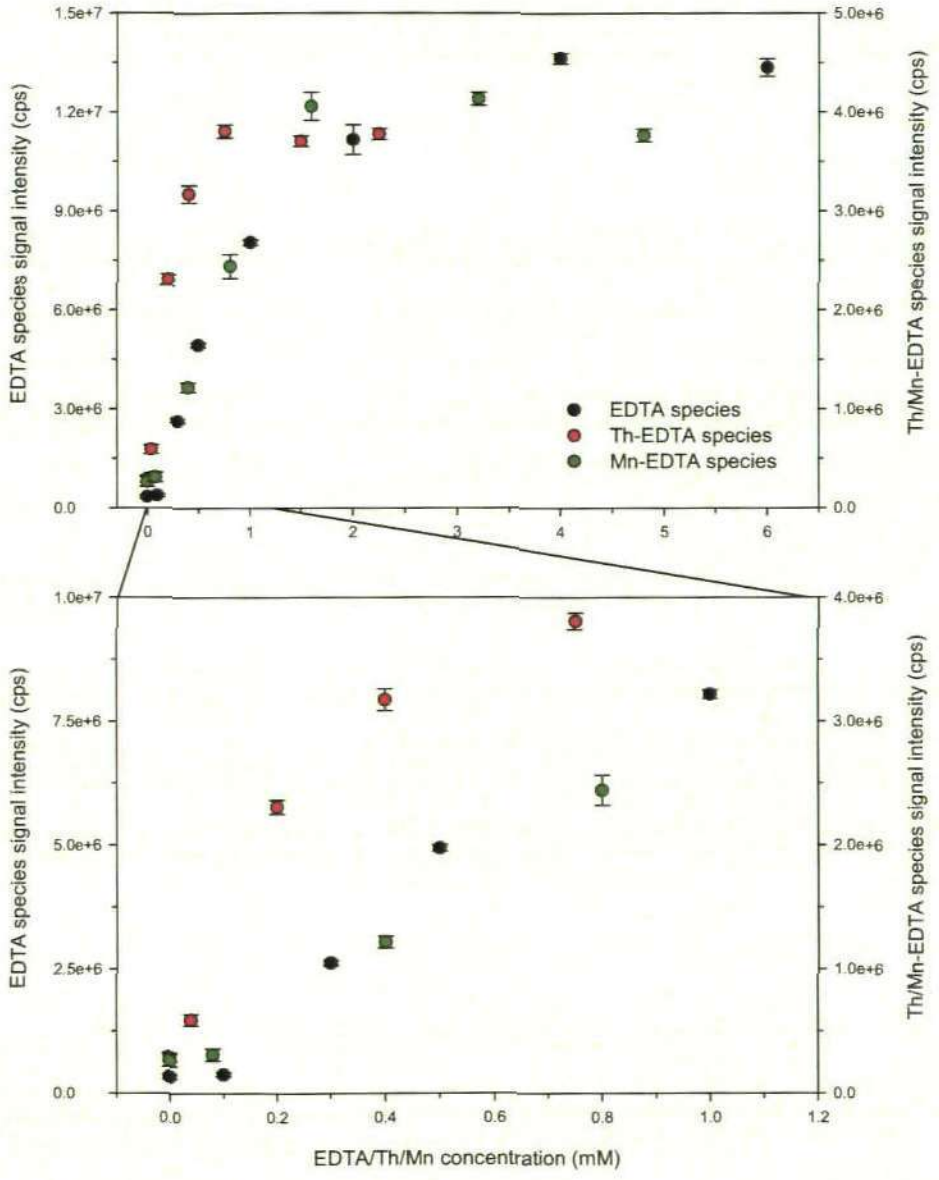

Figure 5. 2 EDTA, Th-EDTA and Mn-EDTA species signal response in ESI-positive ion mode over 0 – 6 mM (top) and 0 – 1 mM (bottom) concentration ranges for EDTA, 1:1.25 Mn:EDTA and 1:2.5 Th:EDTA solutions. The error bars represent ± one standard deviation of 3 replicate measurements (injections).

5.3.2 Signal response for EDTA, Mn-EDTA and Th-EDTA systems

Reproducibility of electrospray response. To evaluate the consistency of the instrument sensitivity, 3 calibration standard solutions over the range 0 – 0.5 mM (for EDTA) containing 1:2.5 Th:EDTA and another 3 containing 1:1.25 Mn:EDTA were analysed at different times after mixing and the responses to the Th- and Mn-EDTA species were compared through the gradients of the calibration graphs (Table 5.3).

Table 5. 3 *Evaluation of instrument response reproducibility for Th- and Mn-EDTA species signal response* over time for 3 calibration standard solutions (0 – 0.5 mM EDTA) containing 1:2.5 Th:EDTA and 1:1.25 Mn:EDTA concentrations. Relative signal (%) is the average of the Mn-EDTA or Th-EDTA signal as a % of the total signal response for all EDTA species (cps) for the given concentrations. Error bounds indicate ± one standard deviation (n = 3).

Time of analysis	Th-EDTA species		Mn-EDTA species	
	gradient	*relative signal (%)*	*gradient*	*relative signal (%)*
1 h	1.06×10^7	67 ± 2	2.72×10^6	70 ± 4
20 h	1.10×10^7	68 ± 7	2.57×10^6	68 ± 4
23 h	1.67×10^6	66 ± 5	1.11×10^6	69 ± 4
27 h	2.33×10^6	74 ± 3	7.06×10^5	73 ± 5
48 h	1.70×10^6	74 ± 4	5.54×10^5	70 ± 4

The results showed significant (an order of magnitude) variations in instrument sensitivity for both species. However, when the relative signal ratios of Th-EDTA and Mn-EDTA species to the total EDTA species were calculated, the percentage species distributions were reproducible between the series and over time, meaning that fluctuations in the instrument sensitivity over time affected all species equally. Therefore, calibration graphs were run before and after each sample analysis.

EDTA quantification. Over the course of this study, 6 solutions containing 0.2 mM Th and 0.5 mM EDTA were prepared and the EDTA concentration was quantified using a single component EDTA calibration graph. This allowed changes in the EDTA electrospray efficiency to be quantified on the addition of $Th(NO_3)_4$ to the solution. In order to compare the actual free EDTA with the concentration calculated from the EDTA signal, it was necessary to make the assumption that all Th-EDTA species have equal electrospraying efficiency. Therefore, the free EDTA concentration was calculated as per Equation 5.1.

$$[EDTA]_{free} = [EDTA]_{added} - [EDTA]_{complexed} \qquad \textbf{Equation 5. 1}$$

Since the $[ThEDTA_2]^{4-}$ signal represented 32 ± 4 % (mean ± 1 s.d.) of the total Th-EDTA species in these solutions, the complexed EDTA concentration was calculated from the 1:1 and 1:2 Th-EDTA species signals using Equation 5.2.

$$[EDTA]_{complexed} = [EDTA]_{as\ ThEDTA} + [EDTA]_{as\ ThEDTA_2} = ([Th]_{added} * signal\ fraction_{ThEDTA})$$

$$+ ([Th]_{added} * signal\ fraction_{ThEDTA_2} * 2\ EDTA\ molecules\ per\ ThEDTA_2\ complex) \qquad \textbf{Equation 5. 2}$$

Thus complete Th complexation by EDTA would leave 0.24 ± 0.01 mM free EDTA (of the initial 0.5 mM) in solution. However, only 0.13 ± 0.03 mM EDTA was measured in the Th and EDTA solutions. The equivalent experiment was carried out for 5 solutions of 0.4 mM Mn and 0.5 mM EDTA, and 0.09 ± 0.01 mM EDTA was detected, which was consistent with complete Mn complexation. Baron & Hering (1998) achieved quantification of uncomplexed and metal complexed EDTA in a Cu-Pb-EDTA (0.4, 0.4, 1 mM respectively)

system using calibration graphs for EDTA only and single metal-EDTA systems, suggesting that the presence of Cl^- and NO_3^- (from the $CuCl_2$ and $Pb(NO_3)_2$ salts) did not have an effect on signal response of the free EDTA and EDTA complexes. However, Mollah *et al.* (2000) observed a decrease in the Fe- and Zn-EDTA signal as the Cl^- concentration increased in solution. In this work, there is the further complication of coexisting 1:1 and 1:2 complexes, so it is difficult to assess the full extent of signal suppression, but the best estimate of the effect of the addition of 0.2 mM Th as $Th(NO_3)_4$ on the EDTA response is that the EDTA signal was suppressed by about 55 %. This suppression factor is applied in the ternary systems described in section 5.3.3.

Signal response in solutions of increasing complexity. To assess the effect of the addition of a second metal/radionuclide salt on the signal responses for complexes, Th- and Mn-EDTA species signals were compared before and after the addition of i) 0.4 mM Mn to a 0.2 mM Th and 1 mM EDTA solution, and ii) 0.2 mM Th to a 0.4 mM Mn and 1 mM EDTA solution. The EDTA concentration was sufficient to fully complex both metals, and thus the signal of the pre-equilibrated complex should not be affected by competition. However, the initial Th- and Mn-EDTA species signals were reduced by 52 and 20 % respectively, further demonstrating the importance of matrix effects as the system becomes more complex. This experiment also identified that the signal for the bis-EDTA complex of Th was reduced by 72 %, compared with 32 % for the [ThEDTA] signal. This could indicate, in keeping with earlier observations and data from May (2009), that the bis complex becomes less viable as the relative free EDTA concentration decreases. However, a similar trend was observed for Mn-EDTA species, with the monomer signal reduced by a much lesser extent than the dimer (3 and 26 % respectively). Since

dimerisation is independent of the metal:ligand ratio, this observation may suggest that changes to the solution phase alter the apparent intra-complex species distribution, i.e. affects different species to differing extents, highlighting the likelihood that different species of Th- and Mn-EDTA complexes will not have the same electrospraying efficiency.

Internal standard addition. The addition of an internal standard could correct for signal suppression and overcome changes in instrument response over time. Wang & Agnes (1999) selected a Ni-EDTA complex as internal standard for Sr-EDTA quantification. However, in this study, the stability constants of the radionuclide/metal–EDTA complexes of interest are higher/similar to Ni-EDTA (log $k_{[NiEDTA]}$ = 20.1), thus addition of Ni would complicate the systems further. Therefore, four low molecular weight organic molecules with low affinity for metals (caffeine, glucose, sucrose and salicylic acid) were investigated as potential internal standards. These molecules have molecular weights in the range *m/z* 50 – 1000 and are ionisable in MilliQ water. When analysed in the positive ion mode, clear signals were identified for caffeine, glucose and sucrose, but not for salicylic acid (Table 5.4). The effect of these molecules on the EDTA signal response was studied by individually spiking 0.1 mM of the three organic molecules to four EDTA standard solutions (0 – 1 mM). The EDTA gradient was not significantly affected, but the linearity of response was reduced in all cases. When the signal ratio of EDTA species to organic molecule was plotted as a function of EDTA concentration, only sucrose did not reduce the R^2 value, making it a potential internal standard. However, in solutions of higher complexity containing 0.32 mM Mn and 1 mM EDTA, the presence of sucrose reduced the EDTA signal by 47 %. A similar effect was observed for Mn-EDTA signals, with 51 % signal reduction. On the other hand, the presence of $MnCl_2$ decreased the sucrose signal by only

10 %, demonstrating again the different effect observed depending on the nature of the species in solution. These results also suggest that the addition of sucrose would not adequately compensate for changes in signal suppression and would add more complexity to the spectra. Therefore, the use of external standards was selected as the preferred approach for quantitative analysis in subsequent studies.

Table 5. 4 Effect of four organic molecules (0.1 mM) on the gradient and linearity of a 4 point EDTA calibration series (0 – 1 mM).

Solution	*m/z* observed for internal standard	EDTA gradient (cps mM^{-1})	EDTA linearity (R^2)	EDTA/organic molecule signal ratio linearity (R^2)
EDTA	n.a.	1.12×10^7	0.9889	n.a.
EDTA + Caffeine	319	1.08×10^7	0.9046	0.4091
EDTA + Glucose	203*, 290	1.24×10^7	0.9862	0.9363
EDTA + Sucrose	365*, 281, 533	1.12×10^7	0.8901	0.9907
EDTA + Salicylic acid	n.d.		n.a.	

n.a. = not applicable; n.d. = not detected in EDTA solutions; **m/z* used for the signal ratio

Signal correction for Th-Mn-EDTA systems. Figure 5.3 summarises the percentage signal suppression identified as the solution complexity increased. In order to use calibration graphs from solutions containing EDTA, Th-EDTA and Mn-EDTA for the Th-Mn-EDTA ternary system, the signals of the standards were decreased by 55, 50 and 20 % respectively. These experiments test the assumption that the signal suppressions are relevant across the concentration range of EDTA used and that the formation of different combinations of species with different EDTA concentrations does not affect quantification. Therefore, the numbers obtained were first evaluated and compared in terms of quantification and their agreement with a speciation model output. Then, acknowledging

the limitations of the analysis, the results were used to infer the competitive displacement processes occurring in EDTA limited systems.

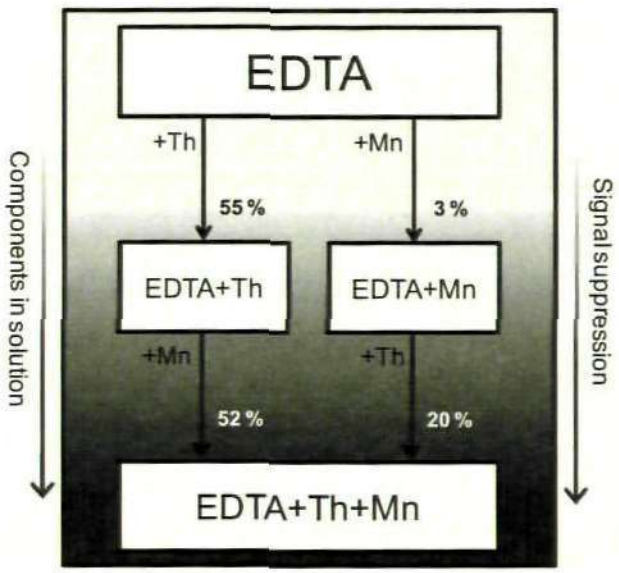

Figure 5. 3 Schematic diagram summarising the ESI-signal suppression with an increasing number of components in solution. The percentages represent the signal suppression for EDTA, Th-EDTA and Mn-EDTA species.

5.3.3 Interactions in the Th-Mn-EDTA ternary system

Kinetics of the complexation reaction. In order to determine the time for complete complexation of Th and Mn by EDTA in the ternary system, the signal intensities of all the species were studied over time. EDTA was added to a solution containing Th and Mn, to give final concentrations of 0.2 mM Th, 0.4 mM Mn and 1 mM EDTA, mixed and flow-injected into the ESI-MS within 1 – 2 min and then at 10, 60 and 1440 min (24 h). The solutions were re-analysed after 22 days. EDTA, Th-EDTA and Mn-EDTA species signal intensities showed a rapid increase in the first 10 min and small intensity changes were recorded up to 24 h (Figure 5.4 top). Higher intensities were observed after 22 days. However, as the instrument response varies from run to run, the relative abundances

were calculated (Figure 5.4 bottom) and showed no significant change after 1 h. Therefore the complexation reaction of both metals was rapid in the presence of excess ligand and equilibrium was reached after 1 h. The last data point (22 days) also demonstrates that Th and Mn did not precipitate over the 22 days incubation time.

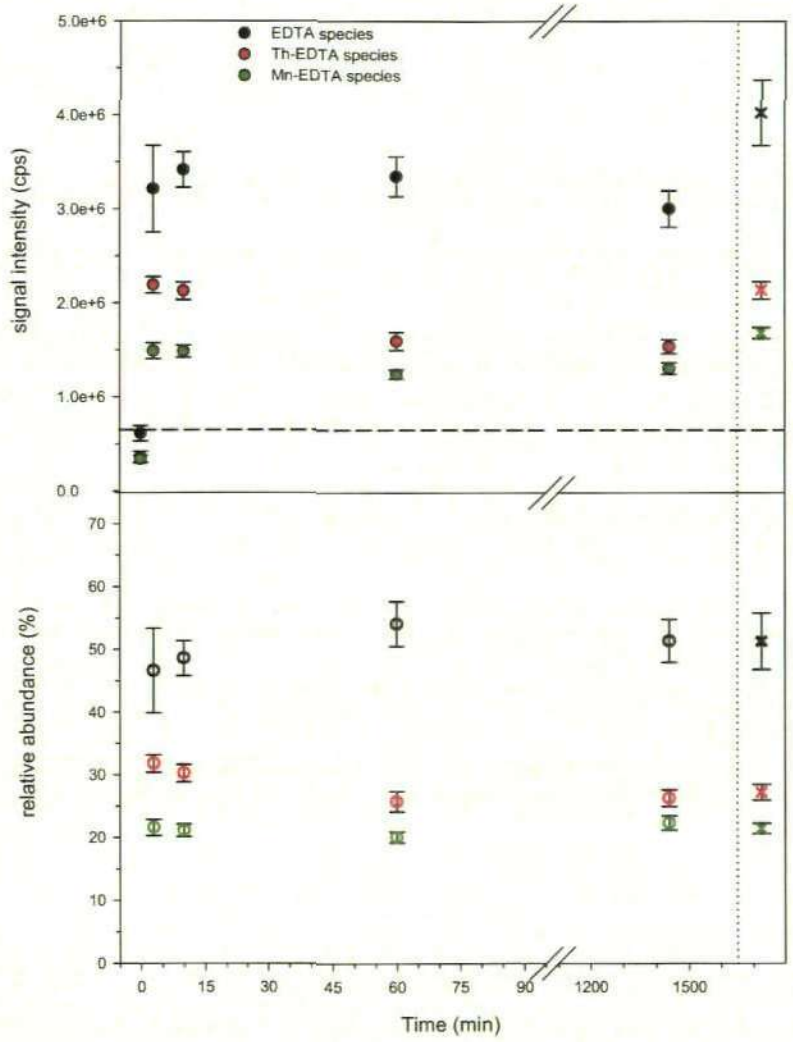

Figure 5. 4 Corrected signal intensities (top) and relative abundance (bottom) over time for EDTA, Th-EDTA and Mn-EDTA species from a solution containing 0.2 mM Th, 0.4 mM Mn and 1 mM EDTA. The crosses represent the 22 day data points and the horizontal dashed line indicates the signal intensity background. The error bars represent ± one standard deviation of 3 replicate measurements (injections).

Quantification of EDTA species and complexes over an EDTA concentration range. The capability of the ESI-MS to quantify Th-Mn-EDTA systems was assessed by measuring the

total EDTA species from three replicate solutions containing 0.2 mM Th, 0.4 mM Mn and four EDTA concentrations (0.25, 0.5, 1 and 2 mM). The solutions were analysed 22 days after mixing. The total EDTA concentration measured in solution, i.e. the sum of free EDTA, Th-EDTA and Mn-EDTA concentrations, was plotted against EDTA concentration (Figure 5.5) and resulted in a linear trend line (R^2 of 0.989) with a gradient close to 1. This suggests that the signal correction applied was reasonable.

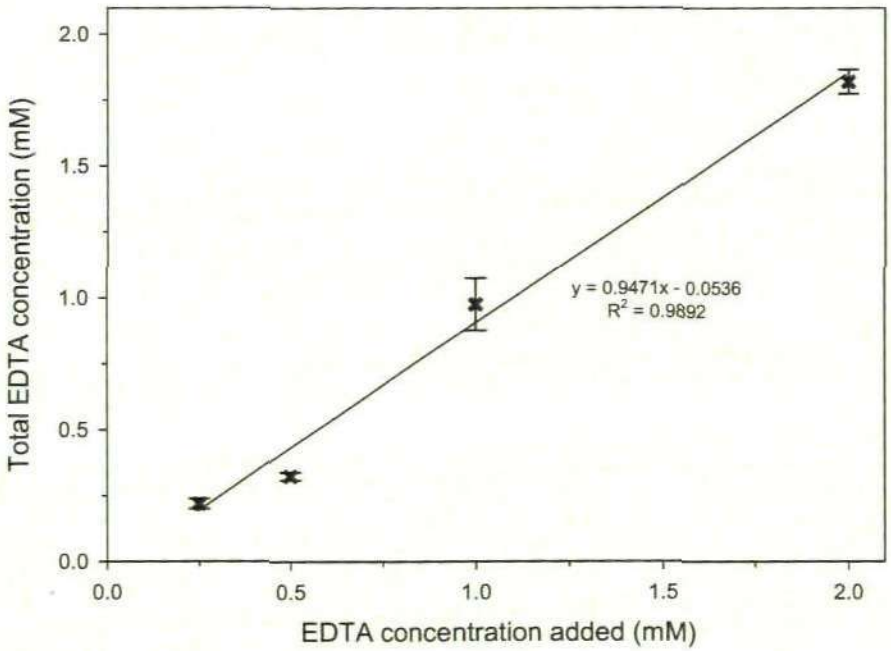

Figure 5. 5 *Quantification of total EDTA concentration in solutions containing 0.2 mM Th and 0.4 mM Mn over an EDTA concentration range. Measurements were obtained after 22 d. The error bars represent ± one standard deviation of 3 replicate solutions.*

The quantification of the individual EDTA species was compared with the output of two speciation models, Visual MINTEQ and HYDRA/Medusa, to assess how well the experimental data agreed with theoretical predictions. All components present in the ternary system were included in the calculations (Th^{4+}, Mn^{2+}, EDTA, Na^+, Cl^-, NO_3^-, pH 3.1). Visual MINTEQ predicted that Th would precipitate when ThO_2 or $Th(OH)_4$ was specified as the possible solid phase. In contrast, HYDRA/Medusa predicted that the

$[Th_2EDTA_2(OH)_2]^{2-}$ dimeric species (log k = 62) would dominate the speciation throughout the pH range. The dimer has been discounted by other authors (Cartwright *et al.*, 2007) when investigating Th-EDTA speciation in the solution phase, therefore this dimeric species, as well as the formation of solid phases, were excluded from the databases for the solution phase speciation calculations shown here. Predicted EDTA, Th-EDTA and Mn-EDTA concentrations were obtained by summing the fractional contributions of the different species predicted by the models before conversion to concentration. Both models gave similar (if not equal) results and thus were considered as one data set during the comparison with the experimental data (Table 5.5).

Table 5. 5 Comparison of model and experimental concentrations of free and complexed EDTA species at different EDTA concentrations (pH 3.1).

Initial EDTA *concentration*	Species predicted by speciation models	EDTA concentration (mM)	
		Visual MINTEQ and HYDRA/Medusa	***Experimental***
2 mM	H_2EDTA^{2-}, H_3EDTA^-, H_4EDTA (aq), H_5EDTA^+	1.40-1.41	1.42 ± 0.04
	ThEDTA (aq), $ThHEDTA^+$	0.20	0.22 ± 0.01
	$MnEDTA^{2-}$, $MnHEDTA^-$	0.39-0.40	0.19 ± 0.03
1 mM	H_2EDTA^{2-}, H_3EDTA^-, H_4EDTA (aq), H_5EDTA^+	0.42	0.36 ± 0.04
	ThEDTA (aq), $ThHEDTA^+$	0.20	0.21 ± 0.01
	$MnEDTA^{2-}$, $MnHEDTA^-$	0.38	0.41 ± 0.06
0.5 mM	H_2EDTA^{2-}, H_3EDTA^-, H_4EDTA (aq), H_5EDTA^+	0.03-0.04	0.00 ± 0.01
	ThEDTA (aq), $ThHEDTA^+$	0.20	0.14 ± 0.01
	$MnEDTA^{2-}$, $MnHEDTA^-$	0.26-0.27	0.19 ± 0.01
0.25 mM	H_2EDTA^{2-}, H_3EDTA^-, H_4EDTA (aq)	0.00-0.01	0.01 ± 0.01
	ThEDTA (aq), $ThHEDTA^+$	0.20	0.10 ± 0.01
	$MnEDTA^{2-}$, $MnHEDTA^-$	*0.04-0.05*	*0.10 ± 0.03*

With excess EDTA (1 and 2 mM), the experimental concentrations of free EDTA and Th-EDTA agreed with the model predictions. However, for the 2 mM EDTA system, the Mn-EDTA concentration was 50 % of that predicted. Cartwright *et al.* (2007) reported a variation of the solution pH between 5.7 and 2.2 over a Th-EDTA concentration range of 0.04 – 2 mM when the solutions were prepared in water. At the lowest pH, the models predicted that 50 % of the Mn concentration would be complexed by EDTA and 50 % would be free Mn^{2+} in solution. Therefore, in the 2 mM EDTA system, a pH shift of 1 unit towards lower pH values would explain the 50 % underestimation of the Mn-EDTA concentration. This rationale cannot be applied to the 0.5 mM EDTA system because the total concentration of Th- and Mn-EDTA species measured was lower than the concentration of added components and thus also lower than those predicted by the speciation models. However, the experimental ratio of Mn-EDTA/Th-EDTA (1.38) agrees with the model prediction (1.32). Since no free EDTA was detected, it suggests that the signal correction was underestimated in this system and hence the assumption of equal signal suppression factor over a concentration range was not completely valid.

With a 0.25 mM EDTA concentration, the model predicted that Th^{4+} would be fully complexed while almost 90 % of Mn^{2+} would remain uncomplexed ($\log k_{[ThEDTA]} = 26.7 > \log k_{[MnEDTA]} = 15.6$). However, experimentally, equal concentrations of Th- and Mn-EDTA were detected. No free EDTA was measured and the total EDTA concentration was within uncertainties of the concentration added, suggesting that quantification of Th-EDTA and Mn-EDTA species was achieved.

Competition in an EDTA limited system. Due to the agreement between the model predictions and the data from the 0.5 mM EDTA competitive system, this system was

selected to examine displacement of the metals from the Mn-EDTA and Th-EDTA complexes in a competitive ternary system. Therefore, the concentration of EDTA, Th- and Mn-EDTA species was measured before, and 22 days after, addition of i) 0.4 mM Mn to a pre-equilibrated solution of 0.2 mM Th and 0.5 mM EDTA, and ii) 0.2 mM Th to a pre-equilibrated solution of 0.4 mM Mn and 0.5 mM EDTA. The total EDTA species and metal complex concentrations before and after the addition of the second metal were within experimental uncertainties (± 5 % RSD) of each other.

Figure 5.6 A shows that the addition of Mn clearly removed the free EDTA from solution, forming Mn-EDTA complexes, but Mn did not displace Th from the EDTA complex. However, Th displaced Mn from the EDTA complex as seen in Figure 5.6 B. These data show that a higher Mn concentration in solution was not high enough to compete for EDTA and the higher Th-EDTA stability constant was the determining factor for the displacement reaction. Furthermore, the similarity of the data at 22 days suggests that the systems had reached solution equilibrium by this time.

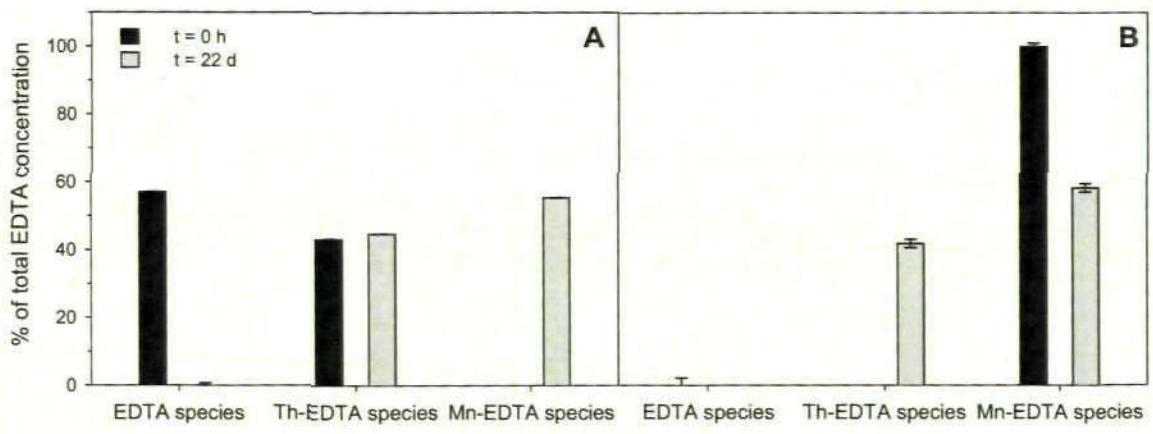

Figure 5. 6 EDTA, Th- and Mn-EDTA concentration, as % of total EDTA concentration in solution, before and 22 days after the addition of **A**) 0.4 mM Mn to a pre-equilibrated solution of 0.2 mM Th and 0.5 mM EDTA; and **B**) 0.2 mM Th to a pre-equilibrated solution of 0.4 mM Mn and 0.5 mM EDTA. The error bars represent ± one standard deviation of 3 replicate measurements (injections).

5.4 Conclusions

ESI-MS has been shown to be a suitable analytical technique for the identification of metal and radionuclide complexes with organic complexing agents in solution. The possibility of identifying all the species from an aqueous solution without prior separation or pH adjustment presents a big advantage; however, the quantification of the species as a function of their electrospray response is a more challenging aspect of the technique. This work has shown that the ESI-response for EDTA, Th-EDTA and Mn-EDTA was linear over a reasonable concentration range (0.1 – 2, 0.04 - 0.75 and 0.08 – 1.6 mM respectively) and that the signal variation from run to run was the same for all the species. However, it has also shown that increasing the components in the solution, e.g. ternary systems, suppressed the signals of the different species to different extents. Therefore, to achieve quantification of species in ternary systems (Th-Mn-EDTA) using single- (EDTA) and two-component (Th-EDTA and Mn-EDTA) systems, a detailed identification and quantification of the signal suppression was needed. Once the signals were corrected, quantification of total EDTA in solution was achieved, and the experimental species concentrations for excess EDTA systems agreed with the model predictions. In competitive systems, suppression factors have to be estimated from non-competitive systems, here, suppression factors from the 1 mM EDTA system were applied to the 0.5 and 0.25 mM EDTA systems. However, the total species concentration measured offered confidence in the suitability of this, and thus the careful approach used allowed the displacement of Mn from the Th-EDTA complex to be observed. Overall, this study has shown that quantification of solution phase interactions on ternary systems using ESI-MS can be achieved after a careful interpretation of the signal responses.

Chapter 6

Conclusions and future work

6.1 Conclusions

The overall aim of this project was to obtain a detailed, mechanistic understanding of radionuclide interactions with organic complexing agents in the solution phase and in the presence of a simple environmental solid phase. It was therefore essential to characterise all components of the systems, thus methods were developed to monitor the behaviour of EDTA, NTA and picolinic acid explicitly. The UV spectrophotometric and IC methods developed were simple and applied widely-available instrumentation, yet allowed compound specific determination over the variable background levels of dissolved organic carbon (DOC). The methods were effective in the presence of natural cations, anions and radionuclides, and the optimised methods presented the necessary analytical figures of merit to be applied in the radionuclide sorption experiments.

Sorption experiments showed that the effect of the ligands on the solubility of the radionuclides is highly dependent on the solid phase used. The natural sand used here was selected for its apparent simplicity and yet the change resulting from moving from pure silica to a matrix that was largely silica was marked. The matrices also resulted in different levels of complexity in the solution phase, as demonstrated by anion and cation desorption and DOC. In the silica system, the presence of EDTA, NTA and, to a lesser extent picolinic acid, showed a clear net effect of increasing Th and U solubility. In the sand system, the sorption of Th and U was kinetically controlled and radionuclide complexation by the ligands enhanced the rate of Th and U sorption, by a mechanism identified as metal exchange with matrix metals. Experiments in which excess EDTA, NTA and picolinic acid (40 – 100 fold) were pre-equilibrated with Th and U (at μM

concentrations) demonstrated that different effects may be observed depending on the order in which radionuclides and complexing agents mix in the environment, and their molar ratio. Pre-equilibration of radionuclide-ligand solutions prior to contact with the sand allowed a greater degree of complex formation for the complexes with slower formation rates (Th and U). This resulted in enhanced rates of Th and U sorption, as the radionuclide complex interacted with the sand surface more readily than uncomplexed Th and U. These results show that complex formation was slow with respect to the interactions with other components of the system, and thus Th and U mobility in this natural sand was reduced under the studied experimental conditions, i.e. radionuclide and ligand concentrations. Furthermore, given that metal exchange was responsible, the results show the importance of competition from matrix metals. In contrast, the complexation of Sr with the complexing agents was rapid and the effect of the ligands was observed as a net effect on Sr solubility (EDTA, picolinic acid) or sorption (NTA). As expected, Cs did not interact with the ligands, and showed rapid sorption kinetics here.

The use of ESI-MS to study competitive interactions in the solution phase (i.e. ternary systems of metal-radionuclide-ligand) presented a challenge in terms of quantification. However, the careful approach taken to determine the signal correction allowed the competitive interactions between Mn and Th for EDTA to be studied at least semi quantitatively. In a limited EDTA system, Th displaced Mn from the EDTA complex even in the presence of a higher Mn concentration, which was consistent with the higher stability constant of the Th-EDTA complex. The work here represents an important step in achieving a protocol for (semi) quantitative interpretation of competitive systems.

Overall, this study has demonstrated the complexity of the mechanisms by which organic complexing agents can affect radionuclide sorption. To appreciate the effect of an organic complexing agent on radionuclide mobility, it is necessary to understand the simple solution behaviour and competition from matrix metals alongside the kinetics of sorption and metal exchange on the solid surface, and the relative attraction of the complex for the solid phase with respect to the radionuclide alone. The results seen here explain the diversity of effects reported in the literature and this study confirms the importance of characterising all components of the system to improve our understanding of the role of ligands in radionuclide migration through the environment.

6.2 Future work

The dune sand used in this study is one of the simplest environmentally relevant soils, and yet the non-silica components altered the effect of the ligands on the radionuclides. Therefore, the effect of the complexing agents on the sorption of Th, U and Sr should be investigated in other types of relevant soil to investigate whether the mechanisms seen here are common to other soils, and the extent to which the kinetic aspects seen here are of widespread relevance. The natural soils should be relatively simple but of contrasting types or of increasing complexity, becoming increasingly organic, clayey or of a more mixed mineral composition.

Metal exchange with sorbed metals was demonstrated to be an important factor for the sorption rate of Th and U, thus competitive interactions in the solution phase using the ESI-MS should be investigated for a wider range of matrix metals. For example, Zn

appeared to be the metal exchanging with Th, therefore Th-Zn-EDTA systems should be studied for different concentration ratios. The kinetics of the complex formation and exchange reactions should be also investigated for ternary systems as this was found to be an important control within the sorption process.

The batch sorption experiments represent a stationary scenario, without groundwater flow. Therefore, laboratory column experiments should be performed using the same natural sand to establish the groundwater flow rates where the changes in sorption kinetics affect the transport of Th and U. Furthermore, in order to asses the effect of the order in which radionuclide and complexing agent reach the environment, two approaches should be taken: i) addition of the ligand after the radionuclide and ii) pre-equilibration of ligand and radionuclide prior to addition to the column.

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